TEXTILE RESEARCH JOURNAL

VOLUME XXIV February, 1954 NUMBER 2

PUBLICATION OF

TEXTILE RESEARCH INSTITUTE

Editorial Office: 10 East 40th Street, New York 16, N. Y.

RHONITE R-I

GIVES STABILITY AGAINST SHRINKAGE IN A WIDE RANGE OF FINISHES

Dimensional stability against shrinkage is a characteristic of modern drapery fabrics finished with the washfast resin, RHONITE R-1.

The product of years of textile chemical research, RHONITE R-1 gives cotton and other textiles a stability that permits frequent washings without shrinkage or loss of their like-new appearance.

RHONITE R-1 produces a lasting beauty in all types of fabrics—plain, calendered or embossed, makes them wrinkle-and-shrinkage-resistant, without harshness or stiffness.

TEXTILE CHEMICALS

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries

RHONITE is a trademark, Reg. U.S. Pat. Off. and in principal foreign countries.

Write or call for complete information about RHONITE R-1—one of the quality chemicals for textile finishing made by Rohm & Haas Company.

TEXTILE RESEARCH JOURNAL

VOL. XXIV, No. 2 February, 1954

In This Issue

The Influence of Applied Forces on the Felting of Wool
A. K. van der Vegt and G. J. Schuringa 99

The Reaction of Wool with N-Bromoacetamide and N-Bromosuccinimide
Christopher Earland and David Raven 108

The Drying Twist in Plant Fibers
Sanford B. Newman and Helen F. Riddell 113

Single Fiber Stress-Strain Apparatus
H. M. Preusser, R. A. O'Connell, A. S. Yeiser, and H. P. Lundgren 118

A Physicist's Approach to Textile Technology
J. W. S. Hearle 123

Device for the Rapid Determination of Tangents to Stress-Relaxation Curves of Single Wool Fibers
W. J. Thorsen 130

A Note on Certain Relationships Between Yarn and Fiber Strain
Milton M. Platt 132

Studies on the Soluble Proteins of the Silk Gland of the Silkworm, *Bombyx mori*
E. H. Mercer 135

INDUSTRIAL SECTION

Static Electricity in Textiles
J. W. Ballou 146

Improvement of Luster of Cotton
Lyman Fourt, Ruth M. Howorth, Marjorie B. Rutherford, and Pauline Streicher

Part V: Fiber Shape in Relation to Luster 156

Part VI: Yarn Structure in Relation to Luster 163

Investigations to Determine the Effects of the Washing Temperature and Time and the Concentration of the Washing Agents when Washing by Machine
Sigurd Köhler 173

Editor: Julian S. Jacobs *Production Editor:* L. Joy Surgent

Associate Editors

H. J. Ball — W. J. Hamburger — H. Mark
Earl E. Berkley — Milton Harris — E. R. Schwarz
Henry Eyring — K. L. Hertel — Kyle Ward, Jr.

TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Entered as second-class matter, April 27, 1945, at the post office at Lancaster, Pa., under the Act of August 24, 1912. Accepted for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. & R. of 1948, authorized May 9, 1950.

Manuscripts and communications should be sent to the editorial office, 10 East 40th Street, New York 16, N. Y.

Subscription rates: $15.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $1.50 each.

Contents copyrighted 1954 by Textile Research Institute. Advertising rates supplied on request.

WANTED

Individual to head Textile Engineering Department and Textile Research Program. Advanced degree desirable, but degrees do not necessarily have to be in Textile Engineering. Experience in research related to the textile industry necessary. Knowledge of fiber technology highly desirable. Salary comparable to similar position in industry. Employment on 12 months basis. All correspondence held in strict confidence.

Reply to
Dean of Engineering
Texas Technological College
Lubbock, Texas

Textile Testing in Germany

Published by T.R.I. in 1948, this report represents a selection of the best techniques for testing fibers, yarns, and fabrics and for service evaluation of textiles as developed in the laboratories of Germany. It brings together a statement of the thinking of the technicians of an entire country in the articles themselves and the bibliographies which supplement them.

Originally priced at $3.50, now offered (a limited supply) at $3.00.

Back Issues of TEXTILE RESEARCH JOURNAL

A few complete sets of back issues and reprints of technical articles of TEXTILE RESEARCH JOURNAL and its predecessor, TEXTILE RESEARCH, are available.

Price, $15.00 per volume.

Textile Research Institute
Publications Department
10 East 40th Street
New York 16, N.Y.

FOR

TEXTILE PROCESSING

LUPOMIN*
A series of cationic nitrogen compounds for softening and finishing textiles.

BENSAPOL*
Liquid detergent derived from Monopole Oil for wool scouring.

ORATOL L-48*
A neutralized sulphonated ester of a higher alkanolamide for increased scouring efficiency.

SULPHONATED OILS
A wide range of types available in numerous concentrations, grades and degrees of sulphonation.

MONOPOLE OIL*
Double sulphonated castor oil for bleaching, dyeing, finishing and as a dispersant for dye solutions.

PARNOL NO. 85
An anionic dodecyl-benzene sulphonate with exceptional wetting properties and high detergent characteristics.

LOMAR PW*
A condensation product of alkyl aryl sulphonates used as dispersing agent for insoluble pigments.

SUPERCLEAR*
Product of natural vegetable gums with complete solubility and outstanding penetrating properties for fine printing.

WETSIT CONC.*
A liquid wetting agent of the alkyl aryl type with rapid wetting and penetrating properties.

HYDROSULFITES OF SODA CONC.
($Na_2S_2O_4$). Reducing agent for vat dyeing.

HYDROSULFITE AWC
($NaHSO_2.CH_2O.2H_2O$). For discharge printing, stripping, and application printing of vat colors.

HYDROZIN
($Zn(HSO_2.CH_2O)_2$). A clear-dissolving, soluble Zinc Formaldehyde Sulphoxylate, for discharge printing and stripping.

GUMS
A wide range of gums including Arabic, Tragacanth, Karaya, Irish Moss, etc. In both liquid and powder form.

*Reg. Trademark

Write for our Chemicals & Specialties Catalog.

JACQUES WOLF & CO.
Chemicals PASSAIC, N. J.
Branches: Carlstadt, N. J. • Los Angeles, Calif.

TEXTILE RESEARCH JOURNAL

VOL. XXIV, No. 2 FEBRUARY, 1954

The Influence of Applied Forces on the Felting of Wool

A. K. van der Vegt and G. J. Schuringa

Vezelinstituut T. N. O. (Fibre Research Institute T. N. O.), Delft, Holland

Introduction

From the results of the research of many investigators it has been established that the felting of wool depends upon a large number of factors. In attempting to arrive at a systematic classification of these factors, it appears that they can be divided into two principal classes—*viz.*, those which are inherent in the material and those arising from the external conditions under which the shrinkage occurs.

Consequently, the following scheme can be made:

Shrinkage Behavior
1. properties of material
   a. structure
      (1) structure of the fabric [2, 7]
      (2) structure of the yarn
   b. fiber properties
      (1) friction [9, 16, 17, 18, 20]
      (2) elasticity [10, 11, 16, 17, 18, 20]
      (3) geometry [6, 16, 19]
2. shrinkage conditions
   a. time [8]
   b. mechanical action [3]
   c. medium [11, 12, 19]

On the whole, attention has been given principally to the relationship between shrinkage and the properties of the fiber, such as scaliness and work of extension. Sookne, Bogaty, and Harris [17, 18] derived from their measurements a definite relation between shrinkage and these properties.

Moreover, it has frequently been investigated to what extent shrinkage depends upon the temperature and the pH of the shaking liquid. This relation can largely be reduced to the aforementioned one, since the medium affects shrinkage through the properties of the fiber [19]. Various investigators noted the influence of the mechanical action during shrinkage [4, 13, 14, 15], which usually led to special efforts being made to keep the mechanical conditions as constant as possible. In their experiments with the wash-wheel, Carter and Grieve [3] paid more attention to the forces involved by examining the effect of the size of the balls used, of the quantity of water, and of the rate of shaking. They did not, however, establish a systematic relationship between shrinkage and mechanical action.

The importance of the forces exerted, however, is clear. Movement of the wool fibers with respect to each other will only take place through external mechanical action; in the event of these movements being partly irreversible as a result of D. F. E. and elastic behavior, they will give rise to felting.

In order to arrive at a better understanding of the phenomenon of shrinkage, it is desirable, therefore, to ascertain the relationship between shrinkage and forces. This may also prove of value for practical purposes, since the divergent practical conditions, such as washing by hand and the making of felt, correspond to widely different force levels.

Method

Most investigators measure shrinkage by shaking a piece of knitted fabric with a liquid and some-

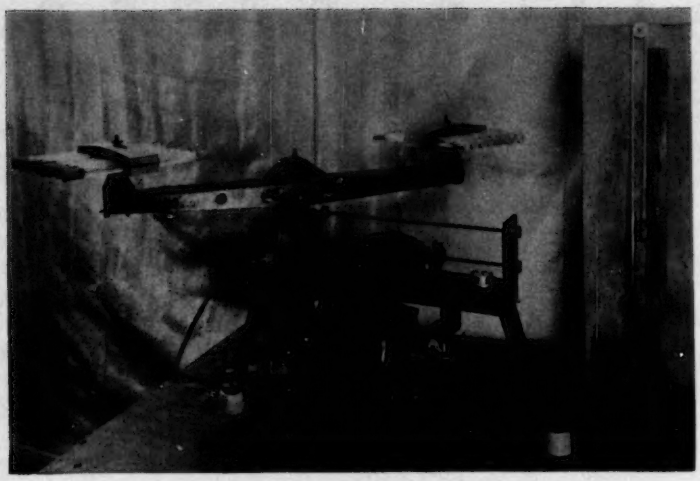


FIG. 1. *General view of the apparatus.*

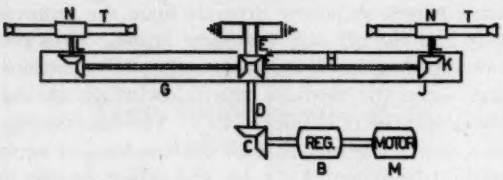


FIG. 2. *Scheme of the apparatus.*

times with the aid of mechanical means in a machine under specific conditions; then the surface shrinkage is determined after a certain time has elapsed.

Instead of knitted fabric, other investigators use top [1] prepared in a special manner or a length of yarn [4, 12].

The use of yarns for these measurements has certain advantages, in that the knitting structure does not enter into consideration, little material is used, and no large equipment is required. Moreover, longitudinal shrinkage can be measured in a reproducible way more easily than surface shrinkage.

In the present experiments, therefore, the shrinkage of yarns was determined. The yarn was shaken in a tube partially filled with liquid. The yarn was attached at the ends of the tube. In order to ascertain the effect of the force exerted, the intensity of the shaking movement was made variable. Distilled water at 20°C was first used as the medium.

Provided the same type of yarn is used each time, the following possibilities present themselves: With constant structure, fiber properties, and medium it is possible to measure the shrinkage-time behavior with reference to the mechanical action. Subsequently, the effect of the yarn structure can be determined by carrying out the same experiments with yarns differing only in their degree of twist.

The effect of fiber properties such as friction and elasticity can be determined by subjecting the initial yarn to various treatments or by varying the medium and subsequently measuring these fiber properties. The present paper gives the results relating to the effect of the forces and to the effect of the twist.

Apparatus

The yarns were shrunk as follows: A 100.0-cm. length of yarn was shaken in a tube (20 cm. long and with an inner diameter of 13 mm.) which was half filled with liquid. The yarn was attached in the rubber stoppers which serve to seal off the ends of the tube.

The shaking movement was achieved with the aid of the following arrangement (Figures 1 and 2). A rotating arm, *G*, is driven by a synchronous motor, *M*, via a shaft, *D*, a transmission, *C*, and a continuously variable-speed control, *B*. The arm is provided with two clamping blocks, *N*, each of which can hold eight tubes and are attached to the shafts, *L*. By means of a stationary bevel gear wheel, *E*, and the transmission elements, *F*, *H*, *J*, and *K*, the shafts are made to rotate in a direction opposite to that of the main shaft, *D*. Conse-

TABLE I. REPRODUCIBILITY OF THE SHRINKAGE MEASUREMENTS

Time (min.)	s_1 (%)	s_2 (%)	s_3 (%)	s_4 (%)	s_5 (%)	s_6 (%)	s_7 (%)	s_8 (%)	$\bar{s}$ (%)	R (%)	σ (%)	$\frac{s}{t}$
0	0	0	0	0	0	0	0	0	0			
1	13.8	12.4	14.6	15.8	14.9	14.0	12.8	13.7	14.0	3.4	1.2	14.0
2	25.3	22.5	25.1	26.5	26.7	24.1	23.1	24.8	24.8	4.2	1.5	12.4
4	40.5	38.7	37.5	40.5	40.6	37.8	39.2	40.0	39.4	3.1	1.1	9.85
6	51.2	47.6	48.0	49.8	49.8	47.8	48.0	50.2	49.0	3.6	1.2	8.2
8	56.5	55.2	54.3	56.3	55.4	53.9	55.1	55.4	55.3	2.6	0.9	6.9
10	61.0	58.7	57.9	59.9	59.8	57.9	58.3	58.8	59.0	3.1	1.1	5.9
12	62.9	61.4	61.4	62.0	61.1	60.5	60.1	61.3	61.3	1.8	0.6	
14	64.3	63.0	62.3	64.0	63.3	62.5	62.9	63.0	63.2	2.1	0.7	
18	65.9	64.8	65.0	65.5	65.3	64.4	64.6	65.2	65.1	1.5	0.5	
22	67.6	66.4	66.0	66.5	66.7	66.2	65.4	67.4	66.5	1.4	0.5	
26	67.7	66.3	66.0	67.2	67.0	66.3	65.7	67.4	66.7	2.0	0.7	
34	68.0	66.3	67.8	67.8	67.6	66.8	67.1	67.9	67.4	1.7	0.6	
											0.9 = $\bar{\sigma}$	

quently, the movement of the blocks, N, with the tubes, T, constitutes only a translation of movement, so that during the movement each tube remains in a fixed direction. As a result of the shaking of the liquid thus achieved, the yarn exhibits longitudinal shrinkage. The shaking conditions can be varied in two ways. With the aid of the control, B, the rotation speed of the arm can be varied between 20 and 270 r.p.m. In addition, the blocks, N, can be placed at three different distances from the shaft, D. The diameter, A, of the circle described can thus be adjusted to 60, 45, and 30 cm., respectively. These two features make it possible to investigate the extent to which the shrinkage is influenced by the force exerted. In the majority of experiments only the speed control is used and the diameter, A, is adjusted to its largest value—*viz.*, 60 cm.

When starting the apparatus, the ultimate speed required can only be attained very slowly owing to the high moment of inertia of the arm with the tubes. Particularly in the case of high speeds, when the shrinkage times are very short (*e.g.*, 10 sec.), this may give rise to incorrect results. For this reason, the bevel gear wheel, E, has been designed so that it can be disengaged. By doing this, the shafts H and L, as well as the tubes, will be stationary with respect to the arm, G, and no shaking movement will take place. The rotating speed of the apparatus can then be slowly raised to the required value; the bevel gear wheel, E, is then engaged by means of a clamping device, and once more disengaged after the required shaking period has elapsed. When the bevel gear wheel, E, is engaged, a revolution counter is put into operation, registering the number of revolutions at which shaking takes place.

The shrinkage is measured by clamping the tube in a vertical position, passing the yarn over a pulley, and reading off the position of the stopper on a graduated scale. This ensures that the yarn is invariably measured under the same tension.

The initial length of 100.0 cm. is adjusted after the yarn has been wetted for ½ hr. so that the relaxation shrinkage is not included in the measurement. After shaking for a certain time, the length of the yarn is again measured, whereupon the yarn is returned to the tube and the shaking resumed. In this manner the shrinkage can be determined as a function of time.

Reproducibility

The reproducibility can be studied with reference to Table I, data for which were compiled arbitrarily from the results of the measurements carried out. The table reports measurements made at a speed of 100 r.p.m. on the untreated standard sample E_o, a 3-ply knitting yarn of 62s grade wool. Columns s_1 to s_8 show the shrinkage of each of the eight yarns, σ being the standard deviation determined with the aid of the range R [5]. The average deviation in this case is 0.9%, so that the reproducibility may be considered satisfactory. In the case of some yarns treated with antishrink agents, larger differences are found, frequently due to nonuniform treatment.

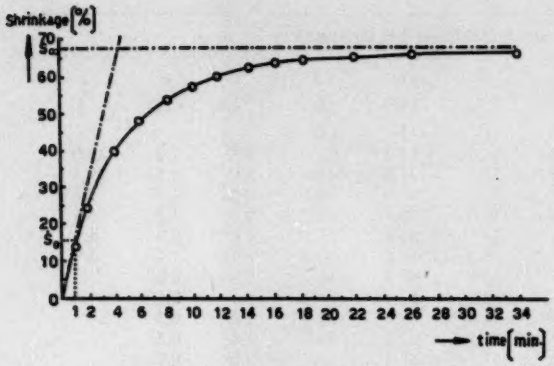


FIG. 3. *Shrinkage, s, as a function of shrinking time, t.*

Parameters

It is advisable to express the results obtained in a simple form. Therefore, it is not sufficient to give the shrinkage after a certain period of shaking, because the course of the curve as a whole would be disregarded. It is possible to express the shrinkage-time behavior by approximation by means of an exponential function of the equation

$$s = a(1 - e^{-bt}),$$

where a and b are the determinative parameters. The measurements, however, frequently exhibit considerable deviations from this equation. It is true that a can be interpreted simply as the limit, but b is not of any direct practical significance. It would therefore be better to express the course of the shrinkage with the aid of the quantities

$$s_\infty = \lim_{t \to \infty} s(t),$$

which is the shrinkage limit, and

$$\dot{s}_o = \lim_{t \to 0} \frac{ds}{dt},$$

which is the initial shrinkage rate (Figure 3).

These values can be determined graphically in a fairly simple manner. The shrinkage limit, s_∞, can be estimated from the graph, if necessary with the aid of a logarithmic time scale. The quantity $\dot{s}_o$ can be approximated by plotting s/t for successive measuring points as a function of t and extrapolating the curve obtained to $t = 0$ (Figure 4).

In this manner we find for the present case that $s_\infty = 70\%$ and $\dot{s}_o = 15.5\%/\text{min}$. These values roughly give the shrinkage behavior as a function of time. In some cases it is found that ds/dt first increases, and then, after reaching a maximum

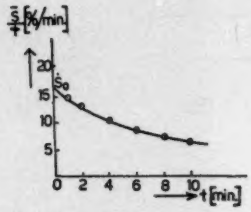


FIG. 4. *Determination of $\dot{s}_o$ from the values of Table I.*

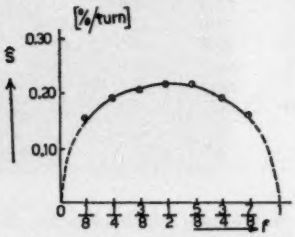


FIG. 5. *Dependence of $\hat{s}$ on quantity of liquid.*

TABLE II. INFLUENCE OF THE QUANTITY OF LIQUID

f	$\hat{s}$
$\frac{1}{8}$	15.3
$\frac{1}{4}$	19.0
$\frac{3}{8}$	20.5
$\frac{1}{2}$	21.4
$\frac{5}{8}$	21.4
$\frac{3}{4}$	18.4
$\frac{7}{8}$	15.8

value, decreases to zero. When this occurs, the value of $\dot{s}_o$ does not represent the initial shrinkage rate, but, rather, the maximum shrinkage. The use of the quantity $\dot{s}_o$ is, however, not yet entirely satisfactory. An increase in the shaking rate not only causes the force to increase, but also the number of times this force transmits an impulse to the fibers in the yarn. It is therefore better not to express the initial shrinkage per unit of time, but per stroke of the apparatus. At the same time the experiments will then correspond more logically with those in which the amplitude of the shaking movement is varied, since this causes a change in the force but not in the number of times this acts on the yarn.

The initial shrinkage per stroke can readily be calculated from $\dot{s}_o/n$, where n represents the number of revolutions per minute. This quantity, which we will denote by $\hat{s}$, can also be derived from

$$\hat{s} = \lim_{N \to 0} \left(\frac{ds}{dN} \right),$$

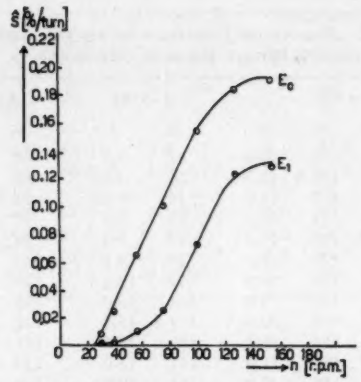


FIG. 6. *Initial shrinkage per turn,* ŝ, *as a function of* n *for an untreated yarn,* E_o, *and a chlorinated yarn,* E_1.

TABLE III. EFFECT OF SHAKING RATE ON THE SHRINKAGE PARAMETERS

	E_o		E_1	
n	$\hat{s}$	s_∞	$\hat{s}$	s_∞
30	0.8	37	0.1	5.5
40	2.4	69	0.2	21
56	6.7	69	1.0	31
75	10.1	70	2.5	40
100	15.4	69	7.3	52
128	18.5	71	12.4	56
156	19.0	70	12.9	60

where $N = nt$, the total number of completed revolutions.

Effect of Quantity of Liquid Used

To ascertain the extent to which the shrinkage is affected by the quantity of water present in the tubes, the shrinkage of the standard sample, E_o, was measured with liquid volumes, f, of $\frac{1}{8}$, $\frac{1}{4}$, $\frac{3}{8}$, $\frac{1}{2}$, $\frac{5}{8}$, $\frac{3}{4}$, and $\frac{7}{8}$ of the total volume of the tube at a speed of 157 r.p.m. With each different liquid volume, the shrinkage of four yarns was measured; $\hat{s}$ was derived from the average results. The values of $\hat{s}$ with reference to the quantity of water are given in Table II and Figure 5. It was found, *inter alia*, that the effect is very slight at about $f = \frac{1}{2}$, which is generally used, so that the measurements of $\hat{s}$ are not affected by small variations in the quantity of liquid. In all these experiments the limit s_∞ remained unchanged at 70%.

Effect of Shaking Rate

The standard sample, E_o, was shaken at various rates and A adjusted to 60 cm. Most measurements were carried out on four or eight yarns at a time, while the parameters $\hat{s}$ and s_∞ were determined from the average shrinkage-time behaviors. Table III and Figure 6 give the values found for $\hat{s}$ as a function of the rotation speed, n, and Table III and Figure 7 give the limits s_∞. It is evident that up to a speed of 100 r.p.m., $\hat{s}$ for E_o may be regarded as roughly proportional to $(n - n_o)$, where n_o represents a threshold value, in this case at 25 r.p.m. Below this value shrinkage does not occur. This threshold is also evident in the course of s_∞ (Figure 7); for $n > 40$ the limit is more or less constant at 70%, while in the neighborhood of $n = 30$ the curve takes a very steep course. Although the investigation in respect of treated yarns is still in progress, the results obtained with another sample, E_1, have been plotted in the same graphs for comparison. E_1 was obtained by chlorination of E_o. With the treated yarn the course is largely analogous, but in this case the threshold in n extends over a fairly large area, which in the course of s_∞ is evidenced by the fact that the curve is considerably less steep; with $\hat{s}$ there is a starting area between 30 and 90 r.p.m.

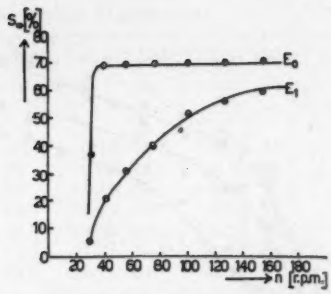


FIG. 7. *Shrinkage limit,* s_∞, *as a function of* n *for* E_o *and* E_1.

Effect of Shaking Amplitude

The same experiments as described in the preceding section were carried out with yarn E_o, but this time with other amplitudes—*viz.*, $A = 45$ cm. and $A = 30$ cm. In most cases only $\hat{s}$ was determined, measuring s_∞ being particularly time-consuming. The values of $\hat{s}$ at different values of A as a function of n are recorded in Table IV and Figure 8. The three curves give the impression that they differ only as regards the scale value for n; when $\hat{s}$ is plotted against log n, it is found that the three curves run approximately parallel. Thus, a multiplication factor for n can be found for each value

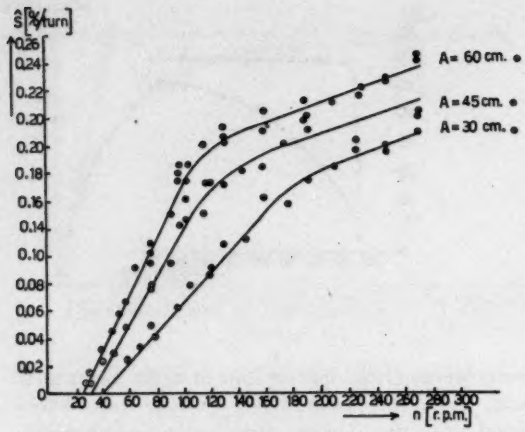


FIG. 8. *Dependence of* ŝ *on* n *for three amplitudes.*

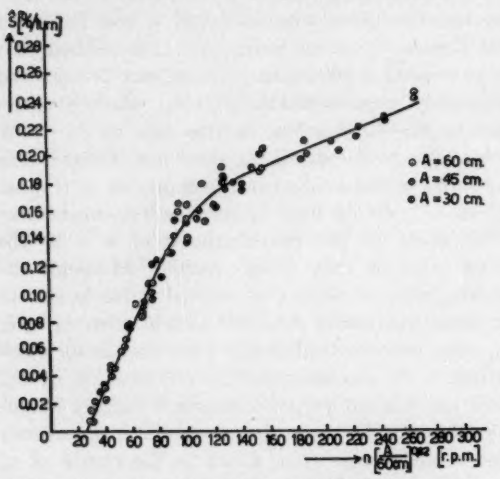


FIG. 9. ŝ *plotted against* $n(A/60)^{0.82}$ *from the measurements of Figure 8 and Table IV.*

of A, so that they merge into each other. It appears that this factor can best be approximated by $A^{0.82}$. Figure 9 shows the result of this transformation. The curves for $A = 45$ and $A = 30$ have both been superimposed on that of $A = 60$ by taking $n(A/60)^{0.82}$ as the horizontal scale value. It follows, therefore, that the shrinkage per stroke depends solely upon this combination of the quantities n and A.

Forces

The actual magnitude of the forces exerted by the liquid on the fibers during shaking is not known, since this magnitude is dependent upon the velocity

TABLE IV. EFFECT OF ROTATING SPEED AND AMPLITUDE ON THE INITIAL RATE OF SHRINKAGE

$A = 60$				$A = 45$		$A = 30$	
n	$\hat{s}$	n	$\hat{s}$	n	$\hat{s}$	n	$\hat{s}$
29	0.8	101	14.0	47	2.8	56	2.25
30	0.8	101.5	16.5	56	4.65	66	3.3
30	1.6	113	18.0	75	7.45	74.5	4.85
39	3.2	115	15.2	75	7.8	77	4.0
40	2.35	127	19.2	89	9.4	94	6.1
46	4.6	128	18.1	96	12.1	103	7.7
52	5.8	128	18.5	101	12.5	117	8.5
52	5.8	156	19.0	114	13.0	118	9.0
55.5	6.7	157	20.4	117.5	15.3	127	13.6
63	9.2	186	19.7	127	15.2	144	11.2
65.5	8.4	187	21.0	141	16.0	158	14.1
74.5	10.1	189	20.0	156	19.0	176	13.7
74.5	10.8	207	21.0	172	18.0	189	15.4
75	9.6	226	21.4	189	19.0	209	16.4
88.5	13.0	228	22.0	269	20.3	224	17.6
95	15.9	246	22.5			224	18.3
95.5	16.5	246	22.7			246	17.9
95.5	15.3	269	24.5			246	17.4
100.5	15.4	269	24.0			269	20.0
						269	18.8

of the liquid with respect to the fibers in the yarn. When there is no yarn in the tube and the viscosity of the liquid is disregarded, the optimum liquid velocity occurring is $2\pi(n/60)(A/2)$ cm./sec., which is proportional to nA. This velocity, however, is modified by the presence of the yarn. This modification is brought about, *inter alia*, by the fraction of the cross section occupied by the yarn, by the movement of parts of the yarn with respect to the tube, and by capillary forces acting between glass, liquid, yarn, and air.

Likewise, little can be said about the nature of the flow, since the flow orifices are of very different dimensions. It is possible that with velocities which are not unduly high, laminar flow conditions will occur, especially when the liquid flows in between the fibers.

In that case, the force is proportional to the liquid velocity. When, moreover, as a first approximation the velocity is assumed to be proportional to nA, it follows that the force, F, equals $nA \times$ constant. This approximation corresponds reasonably well with the result found in the preceding section —*viz.*, that the shrinkage per stroke is a function of $nA^{0.82}$, and with the assumption that it is dependent solely upon the force.

Although the absolute magnitude remains unknown, it is possible to furnish some approximate information concerning the dependence upon number of revolutions and amplitude.

TABLE V. INFLUENCE OF YARN TWIST ON SHRINKAGE PARAMETERS

	m = 200		m = 400		m = 600		m = 800		m = 1,000		m = 1,200		m = 1,400		m = 1,600	
n	$\hat{s}$	s_∞	$\hat{s}$	s_∞	$\hat{s}$	s_∞	$\hat{s}$	s_∞	$\hat{s}$	s_∞	$\hat{s}$	s_∞	$\hat{s}$	s_∞	$\hat{s}$	s_∞
19	0.55															
29	2.7		1.3		0.75		0.23		0.11							
40	6.9	63.5	3.6	62	1.8	55.5	0.82	39	0.32	33	0.18	23	0.05	12	0.025	4
52	9.2	66.5	5.0	65.5	2.5	63.5	1.25	61	0.60	58	0.28	44	0.14	33	0.042	21
76	11.5	67.5	6.0	66.5	3.5	65	1.9	63.5	1.38	61	0.77	59	0.42	55.5	0.22	47
102	13.8	67.5	8.3	67.5	5.0	66	2.9	64.5	1.71	63	1.15	60	0.66	57	0.41	53.5
128	16.4	67.5	10.3	67.5	6.2	67	3.25	65	2.4	63	1.22	59	0.80	56.5	0.59	53.5
158	17.8	67	12.1	67.5	6.8	66.5	4.0	65	2.7	63.5	1.8	59.5	1.15	58	0.81	54
189	18.6	67.5	12.6	67.5	6.7	67	4.9	65	3.4	63.5	2.1	61	1.33	58	0.85	54

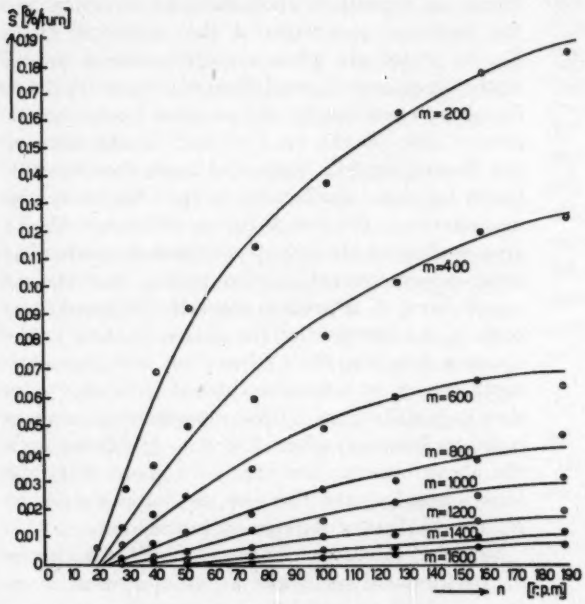


FIG. 10. $\hat{s}$ *versus* n *for different twist parameters,* m.

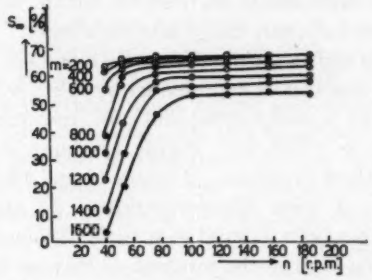


FIG. 11. s_∞ *versus* n *for different twist parameters,* m.

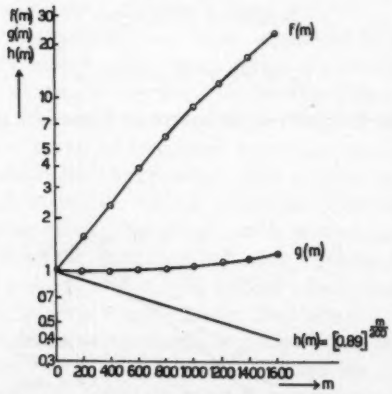


FIG. 12. *The transformation functions* f(m), g(m), *and* h(m).

Twisted Yarns

The object of the preceding experiments was to ascertain the effect of the external forces on the shrinkage. It is interesting to see, however, how the shrinkage changes when the interfiber forces are varied. This may be achieved by using yarns twisted in different measures. To make these yarns the following method was used: The original 3-ply yarn, E_o, was untwisted. A 250-cm. length of the single yarn thus obtained was untwisted and retwisted by giving it a certain number of turns. The number of turns applied, m, was successively 200, 400, 600, 800, 1,000, 1,200, and 1,600. From this twisted single yarn a balanced 2-ply yarn was made by doubling. The 2-ply structures

TABLE VI. SCALE MULTIPLICATION FACTORS FOR s_∞ AND $\hat{s}$

m	$f(m)$	$g(m)$
200	1.56	1.00
400	2.33	1.00
600	3.83	1.01
800	5.90	1.04
1000	8.55	1.06
1200	11.7	1.11
1400	16.7	1.17
1600	23.1	1.25

thus made were used as initial material for a series of shrinkage experiments at different speeds. The results are recorded in Table V and Figures 10 and 11. It is evident from Figure 11 that the upper limit of the values of s_∞ drops somewhat as the twist increases, while, moreover, the threshold moves to higher values of n. In addition to a very steep course of the slopes, Figure 10 also shows this shift. In order to ascertain the nature of these scale changes, the two graphs can be plotted logarithmically; in both cases sets of curves of the same shape are formed, which, by shifting the two axes, can merge into each other. For Figures 10 and 11 the multiplication factors in n are the same, and can be represented by $h(m) = 0.89^{m/200}$; those for s_∞ and $\hat{s}$ ($g(m)$ and $f(m)$, respectively) are shown in Table VI. Figure 12 shows the course of all three functions. Figures 13 and 14 show the results of these transformations. All the curves have thus been reduced to $m = 0$. When we represent the form of the function of Figures 13 and 14 by $P(n)$ and $Q(n)$, respectively, the results may be combined in:

$$\hat{s} \cdot f(m) = P[n \cdot h(m)]$$

and

$$s_\infty \cdot g(m) = Q[n \cdot h(m)].$$

For the first part of the curve in Figure 13 the first expression becomes

$$\hat{s} = c \cdot \frac{h(m)}{f(m)} \cdot \left[n - \frac{n_o}{h(m)} \right],$$

where c and n_o are constants.

Interpretation of the Measurements

The results found give rise to the following observations. In order to displace a fiber in the yarn with respect to the surrounding fibers, it is necessary to overcome frictional forces. These frictional forces are dependent upon the yarn structure and the frictional properties of the individual fiber. During shrinkage, when a specific fiber is moved many times over a small distance, these frictional forces are overcome by the external forces—in the present case by the force exerted on the fiber by the flowing liquid. Since the wool fiber has different frictional coefficients in two directions, the movements in the one direction will invariably be greater than in the other, provided of course that these movements actually occur—*i.e.*, that the external force, F, is greater than the frictional force both in the direction of the scales, R_1, and in the opposite direction, R_2. When $R_1 < F < R_2$, movement occurs in only one direction; in that case shrinkage still occurs. Fiber movement is no longer possible, however, when $F < R_1$. It follows from the above observations that at a speed of n_o the force exerted on the fibers by the liquid is equal to R_1, the smallest of the two frictional forces.

When R_1 increases, either as a result of a change in the frictional coefficient μ_1, or as a result of an increase in the normal forces caused by a change in the yarn structure, the limit shifts to higher n values. The width of the transition area, where s_∞ rises from zero to its constant ultimate value,

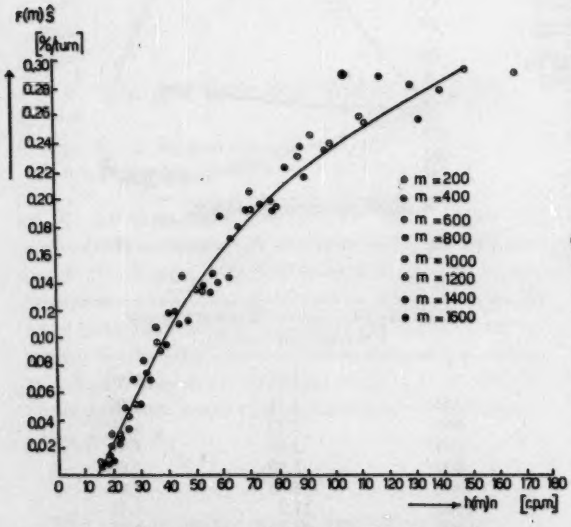


FIG. 13. *Combination of the data of Figure 10 by means of the functions* f(m) *and* h(m).

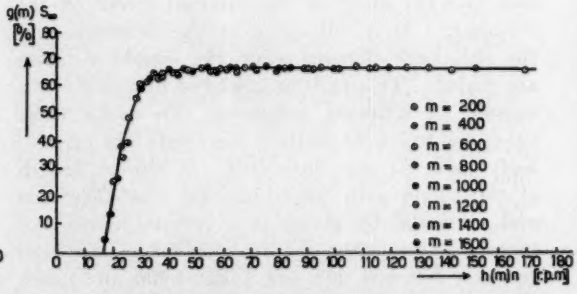


FIG. 14. *Combination of the data of Figure 11 by means of the functions* g(m) *and* h(m).

will probably be dependent upon the deviations which occur in R_1 between the fibers. This tallies with the course of E_1 in Figure 7, since the chlorination is generally not homogeneously distributed over all the fibers. This also explains the widening of the transition area with increasing twist (Figure 11), since—if the relative deviations in R_1 remain the same—the absolute width of the transition area in n will be greater with greater m. By multiplying the n scale by a factor dependent upon m, the curves can, except for a slight difference in level, be made to coincide. The obvious conclusion to be drawn is that the factor $f(m) = 0.89^{m/200}$ denotes the relationship between the course of the liquid forces *versus* speed on the one hand and the course of the frictional force between the fibers *versus* twist on the other hand.

The following can be noticed with respect to the dependence of $\hat{s}$ upon n: when the external force exceeds R_1, the fiber will start to move. The resulting force is then $F - R_1$ (the difference between the static and the kinetic friction being disregarded).

Assuming that F is proportional to n, it is evident from the measurements that the shrinkage per stroke is at first proportional to the resulting force acting upon the individual fiber. Since the fiber moves a short distance during each stroke, it follows that this displacement is proportional to the resulting force.

The factors determining the proportionality constant are still to be investigated. It is clear from the variation in the slopes of the $\hat{s}$-n curves according to the degree of twist that, *inter alia*, the structure of the yarn plays an important part in this connection. The constant c in the equation

$$\hat{s} = c(n - n_o)$$

varies with the degree of twist according to the function $f(m)/h(m)$, attaining for the highest value of m a value of 91.

During the rest of the curve the frictional force in the other direction, R_2, also starts to play a part. Whereas with $R_1 < F < R_2$, fiber movement is only possible in one direction, the fiber will also be able to move in a direction opposite to that of the scales as soon as $F > R_2$. If the magnitude of this movement is again proportional to the resulting force and the same proportionality constant occurs, the resulting movement becomes proportional to

$$(F - R_1) - (F - R_2) = R_2 - R_1,$$

thus being independent of the force.

To some extent this is evident from the measurements. It is true that $\hat{s}$ does not become independent of n, but with a higher value of n the course becomes considerably less steep than with a lower value of n. This representation is, of course, only approximate, and many other factors will also play a part.

Final Observations

The relation between shrinkage and force exerted can be ascertained from the foregoing with sufficient accuracy to gain a deeper insight into the mechanism of shrinkage. Although little is known regarding the factors determining the general course, the threshold which occurs with respect to the force can at least be used as a basis, especially since the position of this threshold can be adequately ascertained when the yarns are twisted. With a view to obtaining further data regarding the shrinkage process, a number of experiments have been carried out with treated yarns and with different media, involving measurements with respect to the frictional coefficients and the elastic properties of the individual fibers.

These experiments are being continued in order that they may be used to correlate the characteristic shrinkage parameters with the fiber properties.

The experiments described herein may also prove useful for practical purposes, since the conditions under which shrinkage takes place in practice are widely divergent as regards the forces occurring.

A standardized shrinkage test is inadequate for determining the shrinkage behavior in these cases, since it only provides information concerning the behavior under a single specific condition.

To enable conclusions to be drawn from the experiments described for practical purposes, it will be necessary to ascertain to what experimental conditions the various circumstances in practice correspond.

Summary

An apparatus and a method have been evolved for measuring the felting shrinkage of yarns at different force values, with good reproducibility.

The course of the shrinkage with reference to time in a specific experiment can be satisfactorily defined by means of two parameters—*viz.*, the initial shrinkage rate and the final limit of the shrinkage.

The effect of the shaking force on the shrinkage appears to be very important; shrinkage does not occur below a certain value of the forces.

Measurements on twisted yarns show that this limit shifts to higher force values when the twist increases; the further course shows that with greater twist the increase in the shrinkage *versus* force proceeds more slowly.

The results obtained may contribute towards the understanding of the shrinkage mechanism, with reference to external conditions and fiber properties.

Literature Cited

1. Bogaty, H., Frishman, D., Sookne, A. M., and Harris, M., TEXTILE RESEARCH JOURNAL **20**, 270 (1950).
2. Bogaty, H., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 895 (1951).
3. Carter, E. G. H., and Grieve, W. S. M., Wool Industries Research Assoc., Special Publication No. 6, Oct. 1944.
4. Creely, J. W., and Le Compte, G. C., *Am. Dyestuff Reptr.* **29**, 292 (1940).
5. Dean, R. B., and Dixon, W. J., *Anal. Chem.* **23**, 636 (1951).
6. Harris, M., *Am. Dyestuff Reptr.* **29**, 387 (1940).
7. Johnson, A., *J. Textile Inst.* **29**, T7 (1938).
8. Le Compte, G. C., and Creely, J. W., *Am. Dyestuff Reptr.* **29**, 387 (1940).
9. Lindberg, J., TEXTILE RESEARCH JOURNAL **18**, 470 (1948).
10. Menkart, J., and Speakman, J. B., *J. Soc. Dyers Colourists* **63**, 322 (1947).
11. Menkart, J., and Speakman, J. B., *J. Soc. Dyers Colourists* **64**, 14 (1948).
12. Mercer, E. H., *J. Council Sci. Ind. Research Australia* **15**, 285 (1942).
13. Moncrieff, R. W., *Textile Mfr.* **77**, 242 (1951).
14. Rath, H., and Fröb, G., *Melliand Textilber.* **32**, 792 (1951).
15. Schofield, J., *J. Soc. Dyers Colourists* **61**, 77 (1945).
16. Sookne, A. M., and Harris, M., TEXTILE RESEARCH JOURNAL **20**, 637 (1950).
17. Sookne, A. M., Bogaty, H., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 822 (1951).
18. Sookne, A. M., Bogaty, H., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 827 (1951).
19. Speakman, J. B., Stott, E., and Chang, H., *J. Textile Inst.* **24**, T273 (1933).
20. Whewell, C. S., and Selim, A., *Nature* **154**, 772 (1944).

(*Manuscript received September 4, 1953.*)

The Reaction of Wool with N-Bromoacetamide and N-Bromosuccinimide*

Christopher Earland and David Raven

Department of Textile Industries, The Technical College, Bradford, England

Introduction

The reaction between wool and organic chloramines has been studied in some detail [1, 2, 4], and it has been shown that certain chloramines react with wool to render it unshrinkable, but only in the presence of high concentrations of hydrogen and chloride ions. In the absence of high concentrations of these ions, the chloramines still react with the wool, which does not, however, become unshrinkable unless very high concentrations are employed. As a result of studies of the reaction mechanism between these compounds and wool, and the properties of the wool after reaction, it has been shown that the assumption that chloramines react with wool exclusively by hydrolysis to free chlorine or hypochlorous acid, depending upon the pH of the solution,

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl,$$

is invalid. Further aspects of this reaction will be discussed in a forthcoming publication.

As an extension of this work, it was decided to investigate the reaction between organic bromamines and wool to determine if they react as simple brominating agents, or if the reaction follows a more complicated course, as with the chloramines. The use of bromine as an antifelting agent has been advocated by Trotman [7, 8] on the grounds that the wool suf-

* These compounds are often included in the general term "bromamines" or "bromoamines" even though they are amide, not amine, derivatives.

fers less damage than with chlorine, but its rapidity of action, leading to unlevel treatment, and its hazardous nature have mitigated its widespread use. It seemed likely that bromamines would overcome the defects of free bromine if their reaction with wool were essentially a slow bromination.

Experimental

Materials

The wool used was a twofold 18s yarn of 56/58s quality knitted into fabric using 12 needles and 18 courses per inch, and cut into 5-in. single squares weighing approximately 5 g. Before use all samples were scoured in a warm dilute solution of soap and ammonia, and were then washed thoroughly in water.

The two bromamines selected for investigation were N-bromoacetamide and N-bromosuccinimide, because these are well-defined, crystalline, stable substances. They were prepared as described by Mauguin [6], by treating a mixture of bromine and acetamide or succinimide with potassium hydroxide solution. For wool treatments, the N-bromoacetamide was purified by recrystallizing from chloroform, after which it contained 111.5% available bromine (theory, 116.0%); N-bromosuccinimide was recrystallized from water, and contained 89.3% available bromine (theory, 89.9%). All reaction kinetics data given in the results section (p. 111), however, were obtained from materials which had been further recrystallized until they contained the theoretical percentage of available bromine. These compounds were analyzed for available bromine by treating a known weight with potassium iodide and acetic acid, followed by titration of the liberated iodine with 0.10*N* sodium thiosulfate solution.

Where possible, all other inorganic and organic reagents used were of "Analar" or B.P. specification.

Wool Treatments and Analytical Procedure

Since each atom of bromine in a bromamine liberates two atoms of iodine from acidified potassium iodide,

$$RNHBr + 2I^- + H^+ = RNH_2 + Br^- + I_2,$$

and all calculations have been based on the relationship

1 liter N-$Na_2S_2O_3$ solution $\equiv$ 79.9 g. bromine,

the quantity of oxidizing agents is expressed in terms of "available" bromine. The actual number of bromine atoms corresponds to half this value. The percentages of oxidizing agents given are based on the weight of conditioned wool containing 14% moisture.

The fabric was wetted out in 1% aqueous Dispersol VL (I.C.I.), washed off, and squeezed. It was then sewn on to a glass stirrer driven at 100 r.p.m. and entered into an aqueous solution of the bromamine. After the bath had exhausted, the samples were washed in cold water and then neutralized in dilute ammonia (1 ml. of 0.880 ammonia solution per 100 ml. of water).

Unless stated otherwise, 5 g. or 10 g. of wool were treated with the bromamine, equivalent to 5.0% available bromine calculated on the weight of fabric, in 0.50% *w/v* sulfuric acid solution at 18°C, using a liquor-to-wool ratio of 40:1. Before the fabric was entered, a 5-ml. portion of the bath was titrated iodometrically using 0.10*N* sodium thiosulfate solution delivered from a microburet. Throughout the treatment the progress of the reaction was followed by iodometric titrations on aliquot portions of the bath removed at intervals of 5 or 10 min. The initial titration ensured that the correct amount of oxidizing agent was in the solution, and allowed calculation of the time for half the active bromine content of the bath to disappear (the half-life). This value is a convenient measure of the rate of the reaction. During the course of these reactions, the solutions developed a yellow color due to the formation of free bromine, which was determined quantitatively by means of a Spekker photoelectric absorptiometer. The instrument was calibrated using solutions containing 0.010%, 0.020%, 0.030%, and 0.040% (*w/v*) of free bromine in 0.50% (*w/v*) sulfuric acid. Three independent calibration curves were obtained during the investigation, and from their reproducibility it was deduced that the free bromine concentrations given are accurate to $\pm$ 0.001%.

Shrinkage Testing and Alkali Solubility

Shrinkage testing was done by hand-milling [3], and the solubility of the wool in alkali was determined by the method of Harris and Smith [5].

Results

Conditions for Rendering Wool Nonfelting

Optimum conditions for rendering wool unshrinkable with N-bromacetamide and N-bromosuccinimide. —In Tables I and II are given the hand-milling shrinkages of samples of fabric after treatment with

TABLE I. EFFECT OF pH AND TEMPERATURE ON THE TREATMENT OF WOOL WITH N-BROMOACETAMIDE

pH of solution	Temperature (°C)	Half-life (min.)	Area shrinkage (%) Treated	Untreated
1.5	18	6	0.8	30.2
3.0	18	20	15.2	30.0
3.0	40	4	25.0	30.4
3.0	60	1.5	21.5	30.4
4.0	18	45	23.0	26.0
5.0	18	60	26.4	26.0
6.0	40	10	26.5	32.2
8.0	50	6	26.4	32.2
9.2	40	18	27.2	32.2
9.2	60	1.5	27.8	32.2

TABLE II. EFFECT OF pH AND TEMPERATURE ON THE TREATMENT OF WOOL WITH N-BROMOSUCCINIMIDE

pH of solution	Temperature (°C)	Half-life (min.)	Area shrinkage (%) Treated	Untreated
1.5	18	3	−2.3	26.5
3.0	18	5	1.1	26.5
3.0	40	2	−2.3	26.5
4.0	18	7	3.8	26.5
5.0	18	12	15.0	27.7
6.0	40	3	17.3	27.7
8.0	40	4	24.1	27.7
9.2	40	15	25.8	27.7
9.2	60	3	29.5	27.7

N-bromoacetamide and N-bromosuccinimide, equivalent to 5.0% available bromine, in solutions of different pH and temperature.

It is seen that, irrespective of the temperature of treatment, the pH is the most important factor for these substances to be effective shrinkproofing agents. Whereas N-bromosuccinimide in solutions of pH as high as 4 reduces the shrinkage of samples to zero, N-bromoacetamide is only partially effective in solutions of pH 3.

Treatment of wool with N-bromoacetamide using reduced amounts of available bromine.—Using the optimum pH of 1.5 (0.50% *w/v* sulfuric acid solution), additional wool samples were treated at 18°C with N-bromoacetamide using reduced amounts of available bromide. Results are given in Table III, which also includes, for comparison, results for treatments using free bromine under the same conditions.

Whereas by using free bromine, 3.0% available bromine effectively reduces the milling shrinkage of wool samples, at least 4.0% available bromine is necessary with N-bromoacetamide.

Properties of the treated wool.—Wool after treatment with either N-bromoacetamide or N-bromosuccinimide, equivalent to 5.0% available bromine, is as white as, or slightly whiter than, similar untreated material, and has a good handle. Immersion in aqueous potassium iodide solution showed that even after thorough washing, treated samples contained residual oxidizing power, and, in practice, an aftertreatment with an antichlor, such as a dilute bisulfite solution, would be advantageous.

Although microscopic examination of milled samples showed that some stripping of scales had occurred, the low figures for solubility in alkali suggests that the damage was restricted more to the surface of the fibers and excessive degradation of the whole fiber had not occurred. The alkali solubilities were 16.5% and 17.4% after treatment with N-bromoacetamide and N-bromosuccinimide, respectively, as compared with 10.0% for similar untreated fabric.

TABLE III. TREATMENTS WITH N-BROMOACETAMIDE USING REDUCED AMOUNTS OF AVAILABLE BROMINE

Available bromine (% on wt. of wool)	Area shrinkage (%) Treated with Br_2	Treated with N-bromoacetamide
0	32.9	28.0
2.0	7.2	—
2.5	—	11.5
3.0	0	8.5
3.5	—	10.4
4.0	4.1	5.7
4.5	—	3.7
5.0	−0.2	3.0

The Nature of the Reaction

Free bromine produced during the reaction.—40 g. of wool fabric was treated at 18°C with N-bromoacetamide, equivalent to 5.0% available bromine, in 1,600 ml. of 0.50% *w/v* sulfuric acid solution. Throughout the reaction the total available bromine and the free bromine in the solution were determined. It was necessary to carry out the reaction on this increased scale to avoid significantly shortening the liquor-to-wool ratio during the reaction, since comparatively large quantities of solution were required for analysis. The duplicate analyses given in Table IV are from different wool treatments.

Table IV shows that during the reaction between wool and N-bromoacetamide, appreciable amounts of free bromine are produced. Thus, after 12 min. the free bromine in solution corresponds to nearly one-fifth of the total available bromine originally present.

TABLE IV. COMPOSITION OF N-BROMOACETAMIDE SOLUTION DURING REACTION WITH WOOL

Time (min.)	Total available bromine in soln. (% w/v)		Free bromine in soln. (% w/v)	
	1	*2*	*1*	*2*
0	0.126*	0.120*	0	0
2.5	0.104	0.104	0.009	0.008
5	0.088	0.088	0.013	0.012
7.5	0.068	0.068	0.018	0.017
12	0.036	0.036	0.024	0.021
15	0.016	0.020	0.016	0.018
20	0.005	0.006	0.004	0.006

* Theoretical value is 0.125%.

TABLE V. THE FREE BROMINE IN A SOLUTION OF 0.108% N-BROMOACETAMIDE AND 0.50% H_2SO_4 IN THE ABSENCE OF WOOL

Time	Bromine conc. (% w/v in soln.)
10 min.	0.0005
20 min.	0.0010
30 min.	0.0015
80 min.	0.0035
2 hrs.	0.0035
3 hrs.	0.0035
5 hrs.	0.0050
72 hrs.	0.0120

It is seen, however, from Table V that the rate of formation of bromine from a solution of 0.108% N-bromoacetamide in 0.50% sulfuric acid at 18°C is extremely slow. This solution was identical with that used for obtaining the results given in Table IV, but in the absence of wool; even after 72 hrs., the quantity of free bromine in solution is only half that formed after 12 min. in the wool reaction.

N-bromosuccinimide is even more stable than N-bromoacetamide in solution, and under the same conditions no free bromine could be detected in a solution of equivalent available bromine concentration after 3 hrs.

Effect of bromide ions on the concentration of free bromine in solutions of N-bromoacetamide and N-bromosuccinimide.—A possible reason for the reaction between wool and N-bromoacetamide producing more free bromine than was produced by the hydrolysis of N-bromoacetamide under identical conditions, but without the wool, could be as follows.

Bromamines are oxidizing agents, and, irrespective of the exact mechanism for oxidizing wool, their available bromine content must ultimately become bromide ions, since wool, even after reaction with chlorine or bromine, is oxidized and contains very little bound halogen. Thus, the over-all reaction between N-bromoacetamide and wool can be represented as follows:

$$CH_3CONHBr + H_2O + W = CH_3CONH_2 + WO + H^+ + Br^-, \quad (1)$$

where W represents the structure of wool.

The bromide ions produced as above will then react with N-bromoacetamide to produce bromine, according to the equilibrium:

$$CH_3CONHBr + H^+ + Br^- \rightleftharpoons CH_3CONH_2 + Br_2. \quad (2)$$

The bromine can then oxidize the wool to produce more bromide ions:

$$W + Br_2 + H_2O = WO + 2H^+ + 2Br^-, \quad (3)$$

so that bromine can be produced by the chain reaction given by equations (2) and (3).

The equilibrium (2) was confirmed by adding different quantities of potassium bromide to solutions of N-bromoacetamide and N-bromosuccinimide in sulfuric acid without wool being present (Tables VI and VII).

It was found also that the bromine-bromide equilibrium (2) is established rapidly, because the bromine concentrations given in Tables VI and VII, which were determined immediately after the KBr

TABLE VI. ADDITION OF KBr TO A SOLUTION OF 0.108% N-BROMOACETAMIDE IN 0.50% H_2SO_4 AT 18°C*

Br^- added as % of Br content of N-bromoacetamide	Free bromine in soln. (% w/v)
6.25	0.011
12.5	0.020
25.0	0.034
50.0	0.055

* This solution would correspond to wool treatments using 5.0% available bromine at a liquor-to-wool ratio of 40:1.

TABLE VII. ADDITION OF KBr TO A SOLUTION OF 0.139% N-BROMOSUCCINIMIDE IN 0.50% H_2SO_4 AT 18°C*

Br^- added as % of Br content of N-bromosuccinimide	Free bromine in soln. (% w/v)
6.25	0.008
12.5	0.015
25.0	0.028
50.0	0.050

* This solution would correspond to wool treatments using 5.0% available bromine at a liquor-to-wool ratio of 40:1.

TABLE VIII. TREATMENT OF WOOL WITH N-BROMOACETAMIDE IN THE PRESENCE OF ACETAMIDE

Acetamide in solution	Half-life of reaction (min.)	Maximum free Br_2 formed (% w/v in soln.)	Time for maximum Br_2 formation (min.)	Area shrinkage of sample* (%)
0	6	0.017	7.5	2.8
M/100	6	0.015	7.5	1.0
M/10	8	0.011	7.5	3.0
M	14	0.006	10	8.5
2*M*	20	0	—	18.4

* Untreated = 28.8%.

was added, remained unchanged after the solution had stood for 30 min.

Effect of acetamide (or succinimide) on the reaction between wool and N-bromoacetamide (or N-bromosuccinimide).—It has been shown in Tables VI and VII that the addition of bromide ions to an acid solution of a bromamine increases the amount of free bromine formed. This is in accordance with the law of mass action, and, by similar reasoning, the addition of acetamide or succinimide should suppress the formation of free bromine. That this is so is clearly shown by Tables VIII and IX, the data for which were obtained from standard wool treatments performed with the addition of different quantities of acetamide or succinimide to the solutions.

Discussion

From the practical standpoint, certain bromamines would appear to constitute a useful class of antifelting agent. N-bromoacetamide and N-bromosuccinimide have high available bromine contents and good stability, and the former is a commercially available chemical. The finished wool possesses very high resistance to milling shrinkage and is of excellent color and handle, and, although microscopical examination of milled samples shows that the surface of the fibers is visibly modified, the alkali solubility test suggests the absence of very severe degradation. Treatment with these agents is best performed in acid solution at room temperature, and under these conditions the process is readily controlled.

Theoretically, the reaction between these substances

TABLE IX. TREATMENT OF WOOL WITH N-BROMOSUCCINIMIDE IN THE PRESENCE OF SUCCINIMIDE

Succinimide in solution	Half-life of reaction* (min.)	Maximum free Br_2 formed (% w/v in soln.)	Time for maximum Br_2 formation (min.)	Area shrinkage of sample† (%)
0	4 (4)	0.016	5	−2.1
M/100	3.5 (3)	0.013	5	0.1
M/10	4 (4)	0.010	5	−0.2
M	5 (5.5)	0.006	5	7.3
2*M*	5.5 (5.5)	0	—	4.1

* In view of the significance attached to these results, duplicate rates are given in parentheses.

† Untreated = 28.7%.

and wool is not simple. While there can be no doubt that at least part of the antifelting action must be due to the elementary bromine produced during the treatment (see Table IV), the initial lack of bromine in the solution and the failure of succinimide, a bromine suppressor, to retard the rate of reaction of N-bromosuccinimide with wool (Table IX) must cast doubts as to whether this is the exclusive mechanism. It is proposed to discuss this mechanism, together with that of the allied reaction between N-chloramines and wool, in greater detail in a later publication.

Acknowledgment

It is a pleasure to acknowledge the interest shown in this work by Dr. F. Happey, Head of the Department of Textile Industries.

Literature Cited

1. Alexander, Carter, and Earland, *J. Soc. Dyers Colourists* **66**, 538 (1950).
2. Alexander, Carter, and Earland, *J. Soc. Dyers Colourists* **67**, 17 (1951).
3. Chamberlain and Menkart, *J. Soc. Dyers Colourists* **61**, 286 (1945).
4. Earland, Ph.D. thesis, London, England, 1950.
5. Harris and Smith, *Am. Dyestuff Reptr.* **25**, P542 (1936).
6. Mauguin, *Ann. chim. et phys.* **22**, 302 (1911).
7. Trotman, *J. Soc. Chem. Ind. London* **52**, 159T (1933).
8. Trotman and Bell, *J. Soc. Chem. Ind. London* **54**, 30T (1935).

(Manuscript received August 19, 1953.)

The Drying Twist in Plant Fibers

Sanford B. Newman and Helen F. Riddell

Testing and Specifications Section, National Bureau of Standards, Washington, D. C.

Abstract

The drying twist of a large number of commercial fibers has been determined. In addition, fibers from related plants which are not at present utilized on a large scale were studied.

It was found that fibers from four of the twenty families represented by commercially important fibers have clockwise drying twists. These were the Linaceae, Urticaceae, Apocynaceae, and Asclepiadaceae. These observations should be useful in fiber identification and in yielding a clue to cell-wall structure.

THE DIFFERENCE in direction of the drying twist in flax and hemp has been exploited in fiber identification by Nodder [9]. Hock [6] noted that flax and ramie have the same direction of drying twist, while hemp and jute twist in the opposite direction. In addition, he related the direction of the drying twist to the spiral structure of the fiber cell wall. However, this relationship has been reported for only a few fibers. When reversals in the spiral wall structure occur, as in cotton, the fiber does not exhibit a unidirectional drying twist [3, 7].

From the limited amount of data available, it would appear that more general information on the drying-twist direction might be useful in a number of applications. It would not only be a helpful tool in fiber identification, but might also yield clues to the cell-wall structure of little-studied fibers. For these reasons it was decided to determine the direction of drying twist in fibers of commercial importance.

A list of fibers available in commercial quantities, published by the American Society for Testing Materials [1], provided a convenient means of outlining the scope of the investigation. However, the data presented here are not strictly limited to fibers on this list. In many cases fibers were available from

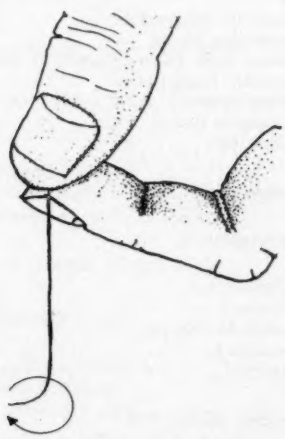


FIG. 1a. *Method of observing the drying twist used by some workers. The point of observation is at the top of the illustration, and the arrow indicates the direction. This is apparently the method used by Hock; the fiber in the illustration would be said by him to have a "clockwise" drying twist. As defined in this paper, however, the direction would be counterclockwise.*

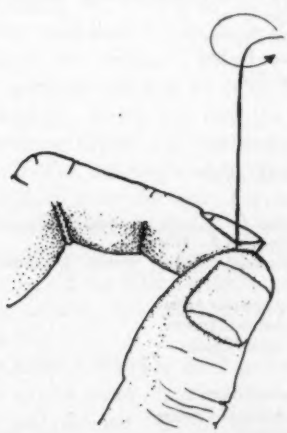


FIG. 1b. *Method of observing the drying twist used to make the observations described herein. The point of observation is at the top of the illustration, and the arrow indicates the direction. This is apparently the method used by Kraus, Plitt, and others. The fiber in the illustration would be said by the present authors to have a "counterclockwise" drying twist.*

TABLE I. FIBERS TESTED FOR DRYING TWIST

Malvaceae
Abutilon theophrasti Medic. (*Abutilon abutilon* Rusby) (*Abutilon avicennae* Gaertn.)
Abutilon trisulcatum (Jacq.) Urban (*Abutilon triquetrum* Sweet)

Palmaceae
Acrocomia fusiformis (Swartz) Sweet
Acrocomia lasiopatha Mart.

Amaryllidaceae
Agave americana L.
Agave angustifolia Haw. (*Agave jacquiniana* Schult. f.) (*Agave vivipara* Auct.)
Agave antillarum Descourt
Agave atrovirens Karw.
Agave brauniana Jacobi
Agave cantala Roxb.
Agave caribaea Hort.
Agave coccinea corata Hort.
Agave coccinea trui Hort.
Agave coccinea brevifolia Hort.
Agave corderoyi Versch.
Agave decipiens Baker
Agave deweyana Trel.
Agave flaccida Jacobi (*Agave cuspidata* Hort.)
Agave fourcroydes Lem.
Agave funkiana Koch & Bouché
Agave kerchovei Lem.
Agave sp.
Agave lecheguilla Torr.
Agave lespinassei Trel.
Agave letonae F. W. Taylor
Agave longifolia Auct.
Agave lophantha Schiede
Agave palmeri Engelm.
Agave pruinosa Lem. (*Agave kellocki* Jacobi)
Agave roezlina Baker (*Agave inghami* Versch.)
Agave salmiana Otto
Agave sisalana Perrine
Agave tequilana Weber
Agave zapupe Trel.

Liliaceae
Aloe sp.

Malvaceae
Althaea rosea (L.) Cav.

Bromeliaceae
Ananas comosus (L.) Merr. (*Ananus sativus* Schult. f.)
Ananas macrodontes E. Morr.
Ananas magdalenae (André) Standl. (*Aechmea magdalenae* André)
Ananas microcephalus Hort.
Ananas pancheanus André
Ananas sagenaria Schult.

Apocynaceae
Apocynum cannabinum L.
Apocynum suksdorfii Greene
Apocynum venetum L.

Araliaceae
Aralia papyrifera Hook.

Gramineae
Arundo donax L.

Palmaceae
Astrocaryum tucuma Mart.

Gramineae
Bambusa sp.

Urticaceae
Boehmeria macrophylla D. Don
Boehmeria nivea (L.) Gaud.

Leguminosae
Brachystegia sp.

Bromeliaceae
Bromelia karatas L. (*Karatas plumieri* E. Morr.)
Bromelia pinguin L.

Moraceae
Cannabis sativa L.

Palmaceae
Chamaerops humilis L.

Tiliaceae
Corchorus capsularis L.
Corchorus olitorus L.

Leguminosae
Crotalaria intermedia Kotschy
Crotalaria juncea L.
Crotalaria spectabilis Roth (*Crotalaria sericea* Retz.)

Asclepiadaceae
Cynanchum sp.
Cryptolepis oblongifolia Regel
Cryptostegia grandiflora R. Br.

Leguminosae
Desmodium leiocarpum G. Don

Palmaceae
Elaeis guineensis L.

Leguminosae
Erythrina herbacea L.

Palmaceae
Euterpe globosa Gaertn.

Amaryllidaceae
Furcraea cabuya var. integra Trel.
Furcraea geminispina Jacobi
Furcraea gigantea Vent. (*Agave gigantea* D. Dietr.)
Furcraea hexapetala (Jacq.) Urb.
Furcraea inermis Drum.
Furcraea macrophylla Baker
Furcraea tuberosa Ait.

Bromeliaceae
Greigia sphacelata Regel

Tiliaceae
Heliocarpus americanus L.

Malvaceae
Hibiscus cannabinus L.
Hibiscus esculentus L.
Hibiscus kitaibelifolius St. Hil.
Hibiscus moscheutos L.
Hibiscus sabdariffa L.

Liliaceae
Hesperaloe funifera (Koch) Trel.

Moraceae
Humulus japonicus Sieb. & Zucc.
Humulus lupulus L.

Malvaceae
Lavatera arborea L.

Linaceae
Linum usitatissimum L.

Malvaceae
Malachra capitata L.
Malva rotundifolia L.

Leguminosae
Medicago sativa L.
Melilotus alba Desr.

Moraceae
Morus sp.

Leguminosae
Mucuna urens (L.) Fawc. & Rendle

Musaceae
Musa ensete Gmel.
Musa paradisiaca L.
Musa textilis Née

Bromeliaceae
Neoglaziovia sp.

Leguminosae
Phaseolus sp.

Palmaceae
Phoenix dactylifera L.

Liliaceae
Phormium tenax Forst.

Leguminosae
Psoralea lanceolata Pursh

Palmaceae
Raphia ruffia Mart.

Liliaceae
Samuela carnerosana Trel.
Sansevieria sp.
Sansevieria ehrenbergii Schweinf.
Sansevieria fasciata Cornu
Sansevieria stuckyi Godefr.
Sansevieria trifasciata Thunb. (*Sansevieria guineensis* Willd.)

Cyperaceae
Scirpus sp.
Scirpus olneyi A. Gray (*Scirpus triqueter* Torr.)

Palmaceae
Serenoa repens (Bart.) Small (*Serenoa serrulata* (Michx.) Hook. f.)

Malvaceae
Sida acuta Burm.
Sida micrantha Schrank
Sida rhombifolia L.

Gramineae
Sporobolus cryptandrus (Torr.) A. Gray

Urticaceae
Touchardia latifolia Gaud.

Tiliaceae
Triumfetta cordifolia A. Rich.
Triumfetta josefina Polak.
Triumfetta semitriloba Jacq.

Typhaceae
Typha sp.

Malvaceae
Urena lobata Cav.

Urticaceae
Urtica gracilis Ait.
Urtica holosericea Nutt.

Leguminosae
Vigna cylindrica (L.) Skeels (*Vigna catjang* Walp.)
Vigna unguiculata (L.) Walp.

Palmaceae
Washingtonia filifera (Linden) Wendl. (*Neowashingtonia filifera* (Linden) Sudw.)

Malvaceae
Wissadula periplocifolia (L.) Presl. (*Abutilon periplocifolium* Sweet)

Liliaceae
Yucca aloifolia L.
Yucca arizonica McKelvey
Yucca baccata Torr.
Yucca elata Engelm. (*Yucca radiosa* Trel.)
Yucca faxoniana (Trel.) Sargent
Yucca filamentosa L.
Yucca glauca Nutt.
Yucca schidigera Roezl (*Yucca mohavensis* Sarg.)
Yucca thornberi McKelvey
Yucca torreyi Shafer
Yucca whipplei Torr. (*Hesperoyucca whipplei* (Torr.) Trel.)

plants belonging to families represented in this list [1], but they were members of unlisted genera and species. They are included in the observations recorded here in order to indicate the taxonomic level at which the drying twist is a characteristic.

Definition

There is some confusion in the literature as to the manner of describing the direction of twist. Hock [6] described the drying direction of flax as "counterclockwise" and of hemp as "clockwise," which contradicts the directions given by others [8, 10]. This confusion results from differences in the methods of observation. The two methods of viewing the specimen can best be demonstrated as in Figures 1a and 1b. In the first case the fiber is held vertically between thumb and forefinger and below the eye level. The rotating end is that part of the fiber most distant from the eye (Figure 1a). The fiber is, of course, held at the end closest to the eye. This is evidently the method used by Hock. Others, however, have held the fiber vertically and below the eye level, but with the free rotating tip closest to the eye (Figure 1b).

Since the latter method is most generally used at present, the drying-twist direction in this work was determined and defined by the method shown in Figure 1b.

Materials and Methods

One of the difficulties encountered in a study of commercial fibers is the problem of obtaining au-

thentic samples which can be related to botantical taxonomic entities. The fiber collection of the National Bureau of Standards and the larger collection of the Bureau of Plant Industry of the U. S. Dept. of Agriculture supplied all of the material studied. Only samples of well-established origin were added to these groups.

All of the fiber plants represented in the collections that were tested for drying twist are included in Table I. In most cases only the genus and species were recorded on the samples; the authors added the names of botanical authorities. Synonyms were found on a number of fiber samples, and these are listed in parentheses in Table I. It is obvious that some fiber plants are represented in these collections several times under different names.

The common and native designations for these fibers cannot always be linked to a single species, and have been avoided in the interests of clarity.

Only bast and leaf fibers were included in the investigation. A number of seed hairs were tested, and, as far as could be determined, appeared to share the bidirectional properties of cotton.

Fibers vary considerably in the rate and amount of activity shown in drying. Whether this is due to age or to method of preparation is not known. Some of the samples were over 50 years old, and exhibited definite drying twists. It did not appear to be a family characteristic, since genera and species of the same family differed greatly in this respect.

The specimen chosen for observation was as fine as possible. One which could just be seen comfortably against a black background appeared preferable. A length of several inches was found to be desirable, but was not always obtainable, and, as a matter of fact, the exact specimen dimensions were often dictated by expediency.

The specimen was held at one end and wetted by dipping in water or running through moistened fingers. It was then observed as shown in Figure 1b. The wetting twist, which is opposite in direction to the drying twist, occurred first. After some seconds, the drying twist occurred. Care must be taken to avoid confusing the two. More elegant methods, which involve the attachment of bits of paper to the rotating tip, were available. These facilitate the observation, but not the specimen preparation, and were usually unnecessary. At least five specimens from each sample were tested.

TABLE II. DRYING TWIST IN FAMILIES REPRESENTED IN A.S.T.M. LIST OF COMMERCIAL FIBERS

Family	Drying twist
Amaryllidaceae	counterclockwise
Araliaceae	*
Apocynaceae	clockwise
Asclepiadaceae	clockwise
Bromeliaceae	counterclockwise
Cucurbitaceae	†
Cyperaceae	counterclockwise
Gramineae	counterclockwise
Leguminosae	counterclockwise
Liliaceae	counterclockwise
Linaceae	clockwise
Malvaceae	counterclockwise
Moraceae	counterclockwise
Musaceae	counterclockwise
Palmaceae	counterclockwise
Tiliaceae	counterclockwise
Typhaceae	counterclockwise
Urticaceae	clockwise

* Composed of short parenchymatous tissue and not suitable for drying-twist determination (*Aralia papyrifera* Hook.).
† Composed of thick interlacing fibers not suitable for drying-twist determination (*Luffa* sp.).

Observations and Discussion

From Table II it can be seen that fibers of species representing only four plant families exhibit a clockwise drying twist. These are the Urticaceae, Linaceae, Apocynaceae, and Asclepiadaceae. All of the species from these families which were examined had clockwise drying twists. The fiber plants included in the American Society for Testing Materials list [1] are members of twenty different families. These plants are not distributed evenly through the families, as some contain only one or a few species. Because these families are of major commercial concern, this investigation was limited to these groups.

It has been shown in at least four fibers (flax, hemp, ramie, jute) that the drying-twist direction is related to the spiral elements of the fiber cell wall [6]. In flax and ramie the majority of spiral elements have an S-twist, and the fiber a clockwise drying twist. Jute and hemp have Z-twisted spiral elements, although the number of spiral fibrils is a small part of the wall content, and a counterclockwise drying twist. Although these are all bast fibers, it has been noted in this laboratory that fiber from leaves of *Musa textilus* Née, which has a counterclockwise drying twist, appears to have the jute-hemp wall structure. When depectinized and swollen, it

displays Z-twisted over nontwisted elements. If the drying twist is determined by the twist of the majority of spiral elements in the cell wall, the jute-hemp type of structure may be quite widespread in plant fibers. A character as basic as cell-wall structure will obviously tend to be a feature of a larger taxonomic unit than species. The drying twist appears to vary at the family level, as noted in Table II.

The term "family" as used here is the "plant family" as defined by Bessey [11]. It is obvious that the Urticaceae of Gray's manual [5], which contains the Moraceae as a tribe, is not sufficiently restricted.

Other types of cell-wall architecture than those described by Hock [6] may, of course, exist. Only two (Apocynaceae and Asclepiadaceae) of the four families exhibiting a clockwise drying twist are closely related. If we assume a mutant origin for this characteristic, then several different mutants are probably involved. Such mutants might not be identical, but only a complete study of the cell-wall structure of this material would reveal the exact situation.

Interestingly enough, members of all four families with clockwise drying twists either have established superiority or received favorable consideration as textile fibers. Besides linen (Linaceae) and ramie (Urticaceae), kendir (Apocynaceae) [2] and various milkweeds (Asclepiadaceae) [4, 12] have been shown to yield bast fiber with excellent textile potentialities.

Fiber strands from collenchyma, epidermal tissues, etc., have not been studied, because these are rarely found in processed fiber. They might, however, cause confusion in working with fresh plants or carefully preserved specimens.

Acknowledgment

The authors are indebted to Sidney F. Blake and Elton G. Nelson of the Bureau of Plant Industry, Soils and Agricultural Engineering, U.S.D.A., for checking the binomials and authorities and for making available a large number of fiber samples.

Literature Cited

1. Am. Soc. Testing Materials, Standard Definitions of Terms Relating to Textile Materials (D–123–51), in "A.S.T.M. Standards," Philadelphia, 1951.
2. Anon., Kendir and Kenaf, *Textile Mfr.* **58**, 411–13 (1932).
3. Denham, J. D., The Structure of the Cotton Hair and Its Botanical Aspects, *J. Textile Inst.* **14**, T86–113 (1923).
4. Dodge, C. R., "Uncultivated Bast Fibers of the United States," U. S. Dept. of Agriculture, Fiber Investigations Rept. No. 6, 1894.
5. Gray, A., "A Handbook of the Flowering Plants and Ferns," 7th ed., New York, American Book Co., 1908.
6. Hock, C. W., Microscopic Structure of Flax and Related Bast Fibers (RP 1482), *J. Research Natl. Bur. Standards* **29**, 41–50 (1942).
7. Hock, C. W., Ramsay, R. C., and Harris, M., Microscopic Structure of the Cotton Fiber (RP 1362), *J. Research Natl. Bur. Standards* **26**, 93–104 (1941).
8. Kraus, W., Fiber Identification Methods, Chap. 22, in "Mathews' Textile Fibers," 5th ed., New York, John Wiley & Sons, Inc., 1947.
9. Nodder, C. R., A Study of Flax and Kindred Fibers, *J. Textile Inst.* **13**, T167–71 (1922).
10. Plitt, T. M., "Microscopic Methods Used in Identifying Commercial Fibers," National Bureau of Standards, Circular No. C–423, 1939.
11. Pool, R. J., "Flowers and Flowering Plants," New York, McGraw-Hill Book Co. 1929.
12. Dodge, C. R., "Useful Fiber Plants of the World," U. S. Dept. of Agriculture, Fiber Investigations Rept. No. 9, 1897.

(Manuscript received September 14, 1953.)

Single Fiber Stress-Strain Apparatus*

H. M. Preusser,† R. A. O'Connell, A. S. Yeiser, and H. P. Lundgren

Western Regional Research Laboratory,‡ Albany, California

THIS PAPER describes a desk-type, autographically recording instrument built especially for precise stress-strain measurements of single fibers, which are tested in a horizontal plane to facilitate measurements in solvent media. The instrument was designed primarily for constant-rate-of-load (stress) testing, but provision for constant-rate-of-elongation testing over a limited range of rates is also incorporated. The mechanical and optical principles used are similar to those used in earlier instruments described by Osumi and Kato [7] and Montcrieff [5]. The present report will facilitate comparison with various other laboratory-constructed and commercial instruments [1, 2, 3, 8], and describes in detail an apparatus that has been used over a period of several years, with uniformly satisfactory performance, in research on the influence of chemical environment on wool fibers [6].

* Presented in part before the Colloid Division of the American Chemical Society at San Francisco, Calif., in April, 1949.

† Present address: American-Marietta Corp., Seattle, Wash.

‡ Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Principles and Design

The principal mechanical components are shown schematically in Figure 1, and the basic electrical circuit is illustrated in Figure 2. Load is applied to the fiber through a twisting torsion wire, and elongation by a moving rack. The load and elongation units are powered separately by two-phase, induction-start, synchronous motors of the type commonly used for constant-speed chart drive in recording instruments. The loading and elongation motions are coordinated by means of a twin photocell activated by a beam of light reflected from a mirror mounted on the torsion wire. The recording chart is mounted on a drum driven by the loading motor; the pen is moved by the elongation motor. By means of a gear shift, the pen displacement may be selected to travel 1, 5, or 10 times the distance over which the fiber elongates.

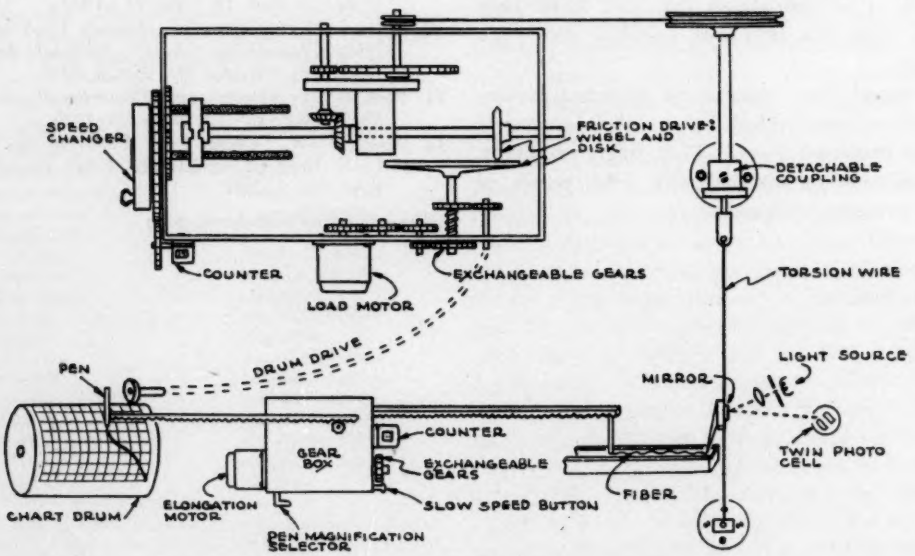


FIG. 1. *Schematic diagram of mechanical components.*

A magnetic gear-changing device independently reverses the pen direction when either edge of the chart is reached. Friction in this system offers no problem, since it is not high enough to affect the rated speeds of the motors.

Either motor can be selected to run reversibly at constant speed while the other acts to preserve balance. The balancing motor is controlled electronically by a "continuous balance" unit * which responds to an unbalance in the photocell circuit. Thus, when testing at constant rate of loading, the twisting torsion wire which rotates the mirror mounted on the lever arm causes the light beam to impinge to a greater extent on the upper cathode of the photocell; the resulting electrical unbalance, properly amplified, directs the controlling power to the balancing motor. The balancing motor, in this case the elongation motor, is activated to compensate for the unbalance in the mechanical system. If the lower photocell cathode receives the greater illumination, as occurs when the load is being removed in the return cycle of a hysteresis loop, the elongation arm is directed inward. For constant rate of elongation, the photocell is switched to direct the loading motor.

A photograph of the instrument is shown in Figure 3. The motor which drives the elongation unit and the pen is shown at the left front; the motor in the back drives the loading unit and the chart drum. The cage-like member seen at the right contains the torsion wire, which is coupled to the large pulley at the rear. The torsion-wire unit is removable at the coupling to permit interchange of units calibrated for different ranges of loading. The optical system is located in the housing at the right; it comprises the light source on top and the photocell at the extreme right. The electronic components are mounted underneath the base plate, with the controlling switches on the front panel.

The fiber to be tested is fastened to two small,

* Brown Instrument Co. The mention of names of firms or trade products does not imply their endorsement by the U. S. Department of Agriculture.

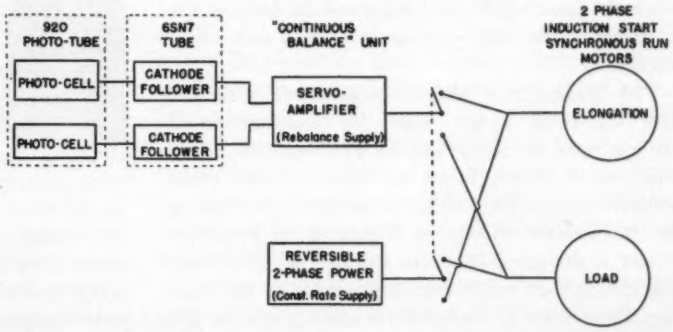


FIG. 2. *Block diagram of control circuit.*

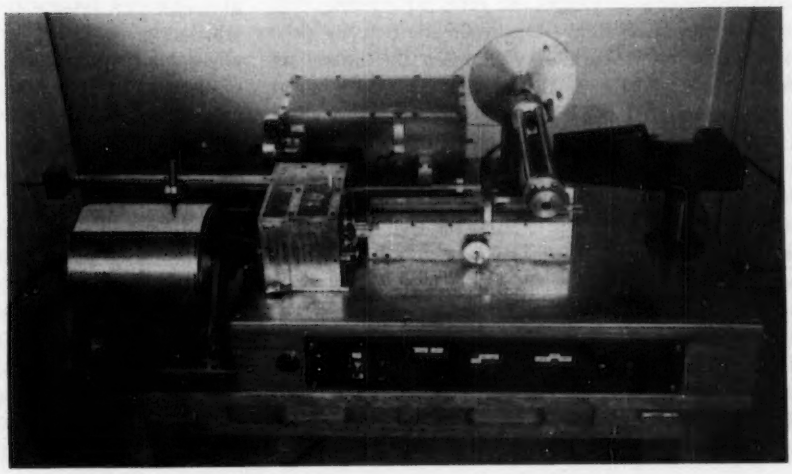


FIG. 3. *Full view of instrument.*

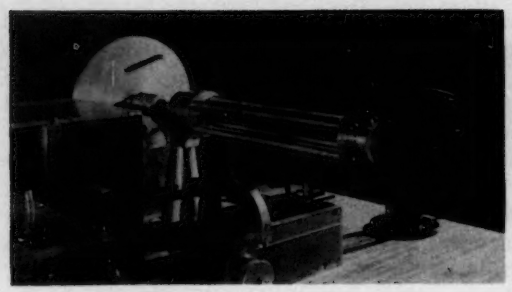


FIG. 4. *Detailed photograph of torsion-wire unit with light source and photocell housing.*

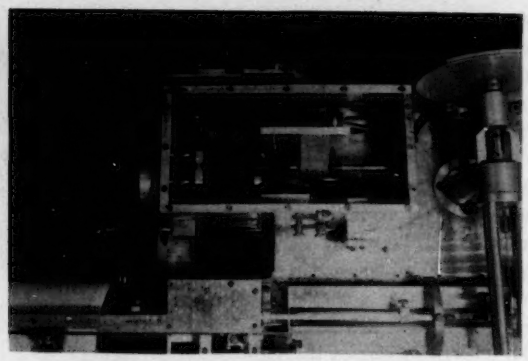


FIG. 5. *Detailed photograph of variable-speed drive for loading mechanism.*

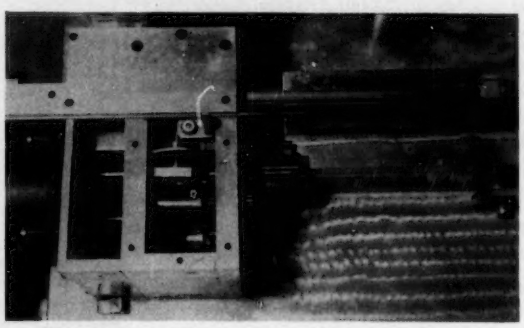


FIG. 6. *Detailed photograph of elongation drive mechanism.*

uniformly cut and perforated aluminum or plastic tabs. One tab is mounted on the elongation arm and the other on the torsion-wire lever arm. When the test is to be performed in a solvent, the bath is raised to envelop the fiber by turning the knurled knob at the front. Limit stops are provided to prevent the lever arm from moving so far as to throw the light beam completely off the photocell cathodes when the fiber breaks. In Figure 4 the torsion wire is visible in the cage with the lever arm and mirror attached.

The loading unit offers a continuous variability over its useful range; thus, for constant-rate-of-loading tests the same rate of stressing can be applied to all fibers, based on their original cross-sectional area. To obtain this variability of loading, the mechanism shown in Figure 5 is employed. Power is delivered from the loading motor through gears, a pair of which are located outside the housing; these may be replaced by other gears to give different stepwise ranges in rates of loading. A variable-speed friction drive inside the housing provides continuous variability between the limits set by the gears. By means of the calibrated speed changer mounted at the left of the housing, the wheel is moved radially along the disk to give the desired rate of loading. The friction disk, which is spring-loaded, may be disengaged from the wheel when the setting is made, so as not to score the face of the disk. Rates of loading of 4 to 80 g./min. may be obtained with a 0.022-in. piano wire; smaller or larger wires may be used to cover other ranges. Power to drive the chart drum is taken from the motor side of the friction disk in such a manner that 10 in. of chart travel takes ½ min. with 1:1 gears and 1 min. with 1:2 gears, etc. With this arrangement the load is recorded directly in stress units or, when multiplied by a factor dependent on speed-changer setting, in grams of force.

Figure 6 shows part of the elongation mechanism. Interchangeable gears on the outside again serve to give different ranges in stepwise rates of elongation, and, since constant-rate-of-elongation tests are usually rates of percentage elongation, the desired rate of percentage elongation per minute may be obtained by adjustment of the sample fiber length when mounting. The motor drive is connected directly to the exterior gears when constant rate of loading is used. When constant rate of elongation is employed, the transmission, located in the right compartment of the box, is shifted in by means of a button to reduce the speed, because the maximum speed of the load mechanism limits response when the sample fiber has a high Young's modulus.

The counter visible on the right side of the gear box indicates the fiber sample length directly in tenths of millimeters when standard tabs are used for mounting. The rack running through the top center of the

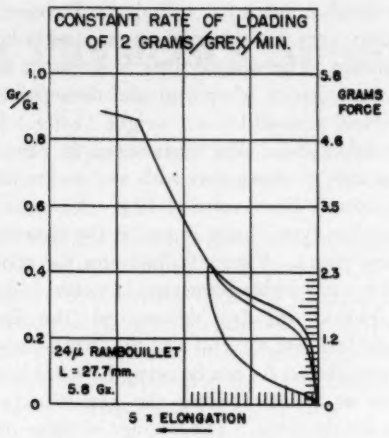


FIG. 7. *A typical constant-rate-of-loading stress-strain curve with one 30% cycle.*

box carries the pen and is linked to the drive through a separate gear transmission in the compartment seen on the left. A lever at the lower left front of the box permits a selection of the transmission gears to attain the desired pen-movement magnification. The pen drive rack is powered by a pinion which can be disengaged to allow pen positioning on the chart.

Switches on the panel permit selection of the motor for balancing as well as direction of rotation of the constant-speed motor. A return switch permits rapid return to the system zero position. A push button permits instantaneous reversal of the constant-rate function as required for recording hysteresis loops. Limit switches are positioned to restrict motion of the load and elongation units at both ends of travel for protection. As mentioned before, pen travel is independently reversed by a magnetic gear shift when the pen reaches contacts at either end of the chart.

For measurements on single wool fibers, which may be between 10 and 60μ in diameter (from about 1 to 35 grex in fineness, requiring up to 65 g. load), we have calibrated three torsion wires made from piano wires of 0.018-, 0.022-, and 0.026-in. diameters. For 10 in. of chart travel, their respective maximum loads are adjustable to 4 to 18, 8 to 34, and 15 to 65 g. of force, depending on the setting of the friction disk drive. In each case the accuracy of loading is within 0.5% of full scale. Calibration is performed by attaching one end of a light thread to the lever arm and then passing the thread over a small pulley which is on jewel bearings. Analytical weights are then hung from the other end of the thread, and the position of the pen on the chart is noted . Gear play is insignificant, and damping by means of a potentiometer adjustment of the voltage on the photocell provides control over hunting; barely perceptible hunting indicates optimum performance. Duplicate stress-strain curves on wet wool fibers which have been permitted to recover between tests are reproducible to within ¼% of full scale.

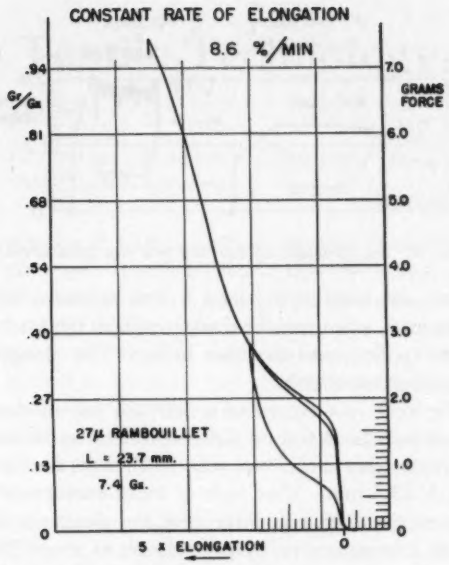


FIG. 8. *A typical constant-rate-of-elongation stress-strain curve with one 30% cycle.*

During 5 years the calibration has not changed perceptibly. Since the wire is automatically reset to zero before each run, any long-term creep or flow effects are eliminated. No mechanical failure has appeared in the instrument; however, design modifications have resulted in some rebuilding, so that some of the moving parts have not been long in use. Electronic components of course require occasional replacement.

Examples of Results

Figure 7 shows a typical stress-strain curve for a Rambouillet wool fiber tested in water at a constant rate of loading of 2 g./grex/min., based on the original diameter of 5.8 grex as measured vibroscopically [4]. It was loaded, therefore, at a rate of 11.6 g./min., and, since the chart moved at a rate of 10 in./min., each inch of chart travel corresponds to 0.2 g./grex, or 1.16 g. of force. The fiber was loaded until

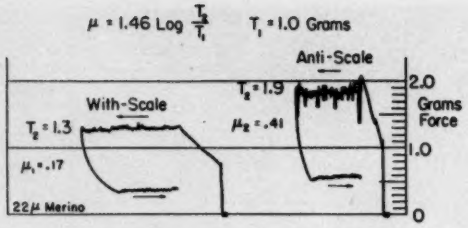


FIG. 9. *An example of surface friction measurement.*

it had extended 30%; then it was unloaded at the same rate; when zero load was reached, the load was again applied until the fiber broke. The elongation magnification was 5 ×.

Figure 8 is a record of a constant-rate-of-elongation stress-strain test on a Rambouillet fiber in water. The extension in this case was 8.6%/min., the sample length 23.7 mm. One inch of chart travel was set to correspond to 1 g. force with the elongation rate set at 2.04 mm./min. An extension of about 25%/min. for a wool fiber is the practical limit for this instrument; at higher rates the load mechanism would lag in the Hooke's law region.

Other Applications

Fiber Creep Measurement

The chart drum is mounted on a pivot and is driven by a wheel against which it rests. If the chart drum is raised slightly and rested on another wheel driven by a slow-speed motor, the chart can then be driven as a function of time. A sample fiber can then be loaded to any desired load and the loading unit switched off; the elongation unit is still controlled by the balancing section, and a record of elongation *vs.* time (creep) results.

Surface Friction Measurement

The surface friction of single fibers can be measured by a slip-stick method, using the capstan principle, in which a small felt cylinder is fastened to the elongation arm as the surface around which the fiber passes. The sample fiber is mounted as usual to the torsion-wire lever arm and then passed over the felt, and a small known weight (1.0 g.) is hung on the other tab. The instrument is switched to constant rate of elongation with any convenient load setting, usually 10 in. equal to 10 g. A constant-rate-of-elongation type of test is run at the slowest speed (0.9 mm./min.). Figure 9 illustrates the results obtained for a wool fiber immersed in water. "Against-scale" friction was first determined; the fiber was then switched end for end and the "with-scale" friction determined. As can be seen, the force builds up, and then at a critical force the fiber slips and the force suddenly drops. The average of these slip-stick peaks permits an estimate of the critical force from which the coefficient of friction is readily calculated.

Acknowledgment

The authors wish to express their appreciation to Mr. Ernest Aeschlimann for his contributions to the design of the apparatus, and to Mr. Aeschlimann and Mr. Jacob C. Jacobsen for their mechanical services.

Literature Cited

1. Ballou, J. W., *ASTM Bull.* No. 150, 38 (1948).
2. Burr, G. S., *Electronics* **22**, No. 5, 101 (May 1949).
3. Dart, S. L., and Peterson, L. E., TEXTILE RESEARCH JOURNAL **19**, 89 (1949).
4. Gonsalves, V. E., TEXTILE RESEARCH JOURNAL **17**, 369 (1947).
5. Montcrieff, R. W., *Fibres* **9**, 170 (1948).
6. O'Connell, R. A., and Lundgren, H. P., TEXTILE RESEARCH JOURNAL (in press).
7. Osumi, G., and Kato, E., *J. Textile Inst.* **28**, T129 (1937).
8. Stein, R. S., and Schaevitz, H., *Rev. Sci. Instruments* **19**, 835 (1948).

(Manuscript received August 4, 1953.)

A Physicist's Approach to Textile Technology

J. W. S. Hearle

Department of Textile Industries, College of Technology, Manchester, England, and School of Textiles, Clemson College, South Carolina

THIS PAPER is concerned with the approach which the physicist can make to problems in textile technology. It is written from the point of view of a physicist, but is not intended to be a dogmatic statement, and certainly others will approach the same problems in different ways. Discussion of the issues may lead to a greater unity of view.

The Purpose of the Physicist

We may start by considering the purpose of physicists in the textile industry, and the justification for their presence.

Their main purpose is to provide explanations of the properties of textiles and of their behavior in processing. This may often be done by the application of existing physical knowledge, but in other cases it will require new developments. For example, the idea of the arrangement of long-chain molecules in crystalline and amorphous regions, a state of matter having peculiar properties of its own, has largely been developed under the stimulus of textile and related research. Or, to take a less developed subject, the full explanation of static charges in textiles will involve the working-out of the general problem of static electricity, which is a backwater left behind by the main stream of development in physics.

Then, through the increased understanding of the properties and processes, the application of physics should lead to improvements in methods and products.

The Present Opportunity

With the development of new fibers which give the possibility of varying properties and dimensions, the need and the opportunity for this sort of work have become much greater.

From prehistoric times until the end of the last century, the textile industry was limited to natural fibers. De Witt Smith in his stimulating lecture "Textile Fibers; An Engineering Approach to Their Properties and Utilization" [1] divided these fibers into six types: wool-like fibers; silk-like fibers; cotton-like fibers; soft bast fibers (*e.g.*, flax); hard bast fibers (*e.g.*, sisal); mineral fibers (*e.g.*, asbestos).

Anyone working or experimenting with fibers was limited to these six types, with their characteristic properties and dimensions.

Insofar as there were improvements in fiber properties, and the change was small, this was the era of the agriculturalist.

Then, starting about 1880 and still continuing, came the era of the chemist, who found new ways of producing fibers—first merely by imitating nature (the age of artificial silk) and later by producing quite new fibers. This was a period of the haphazard creation of fibers, partly because the properties of the fibers produced by the chemists could not be controlled, but also because the textile industry did not know what properties it wanted in a fiber.

We are now passing into a new period, in which we must solve the two problems of producing fibers of given properties and deciding what properties are wanted. De Witt Smith spoke of "the future in which the only real limitations on the variety and the characteristics of textile fabrics will be the ability of the textile technologist to help the fiber maker understand what kind of fiber he wants." This he described as "an engineering job," but I think that it is primarily a problem in physics.

On the processing side there is the same sort of historical development. The era of the craftsman was followed in about 1750 by the age of the engineer, with the introduction of mechanical power, and later instrumentation and automatic methods, but with little change in the fundamental processes. Today the need is for a real understanding of these processes—a physical problem.

The Physicist's Method

Having a purpose to fulfill, and faced with the present opportunity, what method should the physicist adopt?

There is always a temptation to choose what may be called the "pure science" attitude, and to seek justification in W. L. Balls' dictum that "any knowledge about a useful thing must eventually itself be useful" [2].

There is much to be said for this point of view; many great developments have come as a result of it. Until one has some knowledge of a subject, one cannot see what improvements are possible. But it is worth considering whether a planned approach may be more valuable.

Practical Approaches

Practical investigations may be distinguished in various ways. For example, there is the distinction between the observational method of natural history and the experimental method of science. In the former method, the investigation is limited to an examination of the material in the form in which it naturally occurs, and to a description of it—for instance, fibers are examined and their morphology is described. In the latter method, changes are made in the system and their effects are observed; this method is available for most investigations in textile technology.

Probably the most important distinction in the investigations of textile technology is between a statistical and a specific approach. When physics is dealing with simple materials, the specimens used and the conditions of the experiments can be carefully controlled so that highly accurate, reproducible results can be obtained. But, when dealing with natural or industrial products and processes, unavoidable variations are introduced. In order to deal with this variability, statistical methods have been introduced for the evaluation of experimental results. In textile technology there is a place for both specific and statistical investigations, and it is useful to consider some of the factors affecting the choice of method.

For some purposes a statistical investigation is essential; this is usually the case when it is desired to compare magnitudes of results. For example, to determine whether some change in processing procedure results in an improvement, enough tests must be carried out to see if the difference is significant. More tests are necessary the smaller the difference involved. However, a careful selection of specimens or experimental conditions may reduce the variation, and so decrease the number of tests needed.

To investigate the form of a relation between two variables, specific experiments, with fewer tests spread over a wide range of conditions, are more useful, where sufficient constancy of control can be maintained. They are easier to interpret theoretically, particularly if the effect of other variables is included. Statistical tests may blur the fine details of behavior.

Statistical testing may be used to obtain correlations between the various factors involved in the material or process. This introduces several dangers. Apart from the obvious one of fortuitous correlation between unrelated quantities, there is a danger that the correlation may be affected by the selection of samples or the conditions of the experiment. To take an extreme case, different relations are obtained between strength and fineness within a given variety of cotton and between varieties. Another example is that at low humidities static charge may increase as the humidity increases, but at higher humidities it decreases; different mechanisms are limiting the charge.

There are other, more practical considerations which influence the choice of method. One of these is the time available for testing. This consideration leads to the development of tests which can be carried out easily and rapidly, and which may, by the use of a large sample, eliminate the effects of statistical variation and the tedium of single-fiber testing. In doing this, one loses some useful information about variability, and may introduce other effects dependent on the test method. Form factors depending on the arrangement of fibers in the sample may affect the results, and may themselves vary with the way in which the operative prepares the sample. It is then difficult to relate the results of such a test to the fiber properties. This type of test could hinder the development of a real understanding of textile fibers and structures.

All of these advantages and disadvantages should be considered in choosing an experimental program. Statistical methods have much to offer, but should not be allowed to obscure the value of more carefully selected and controlled experiments where these are possible.

Theoretical Approaches

In systematizing and theorizing about experimental results, physics has three main approaches: (*a*) empirical approach, the expression of experimental results in terms of some general relation, which in

its highest form becomes a "fundamental" law of physics, and the basis of more detailed theories of particular phenomena; (*b*) the consideration of energy relations, including such special branches as thermodynamics and statistical mechanics; (*c*) mechanistic approach, concerned with structure and forces.

The example of a simple pendulum will make clear the distinction between the three approaches. One could carry out experiments on many simple pendulums, and find that they all fitted (to a certain degree of accuracy) the relation that time of swing is proportional to $\sqrt{\text{length of pendulum}}$. This would be an empirical approach.

Alternatively, one could consider the energy relations involved, the changes in kinetic and potential energy, and from that deduce something about the motion of the pendulum.

Finally, one could consider the geometry of the system and the action of the force of gravity, and from this work out the motion of the pendulum. This would be the mechanistic approach.

In practice, the three approaches may not always be kept separate; better progress may come from a combination of ideas.

We now consider the application of these three approaches to textile problems.

Empirical approach.—As an example of this approach, there is the relation, which holds for many fibers over a certain range, between electrical resistance, R, and moisture content, M:

$$\log R = -n \log M + \log K,$$

where n and K are constants characteristic of the specimen.

In general, however, the properties of textile materials are complicated, and we do not get the simple relations found for other materials—relations like Boyle's law, Hooke's law, Ohm's law, which can be characterized by simple physical constants. Actually, in any material these laws only hold until experiments are carried out which are accurate enough to detect the deviations, but in textiles the deviations are large and the relations become very complicated. Unless an empirical relation simplifies and generalizes the experimental data, it fails in its purpose.

Thus, the empirical approach is limited in value, when applied to the problems with which we have to deal. It may be just as simple to look at the actual experimental data as to look at the empirical relations which would be necessary to describe them.

Energy considerations.—This may take various forms depending on the level which one is considering—whether it be the energy of electrons, atoms, molecules, or lumps of matter.

On the macroscopic level, thermodynamics can be applied. The advantage of thermodynamics is that its results are certain; its disadvantage is that its results are limited. The two laws of thermodynamics may be written as one equation, so that one cannot obtain more information than is given by the application of this one equation to the problem.

There is a particular snag about the application of thermodynamics to textile materials—thermodynamics only gives *equalities* between equilibrium states; in other cases there are *inequalities*. Textile fibers cannot necessarily be assumed to be in equilibrium states. If one thinks of a fiber as made up of crystalline and amorphous regions, then the reason that crystallization has not proceeded further is not the balance of the actions of energy and entropy, but rather the fixing of the long-chain molecules in positions in which they are tangled up and are not free to move and crystallize further. If by some means we were able to line the molecules up better, we should get another state of lower energy, which would be nearer the true equilibrium state. Nature can do this to some extent—native cellulose fibers have a greater proportion of crystalline material than regenerated fibers. Thus, ordinary cellulose is only in a metastable state—metastable because the molecules are not free to move to the true equilibrium state (Figure 1). Any change in the substance due to mechanical deformation, absorption of moisture, rise of temperature, or some other cause is liable to change this metastable state to some other metastable state. Since one is thus dealing with changes between nonequilibrium states, any application of ther-

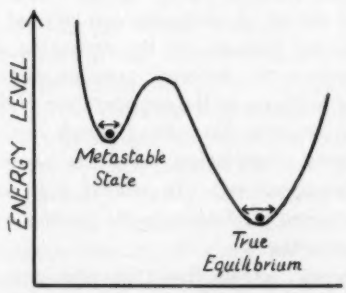


FIG. 1. *True and metastable equilibrium.*

DEVELOPMENT OF TEXTILE FIBERS AND TECHNOLOGY

		PREHISTORIC		
Agriculturalist	Natural fibers		Hand processing	Craftsman
		1750	Mechanical modification	Engineer
Chemist	Artificial fibers	1880		
		1950 ?		
Physicist	Fibers of specified properties		Study of processes	Physicist

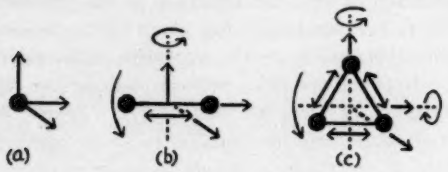


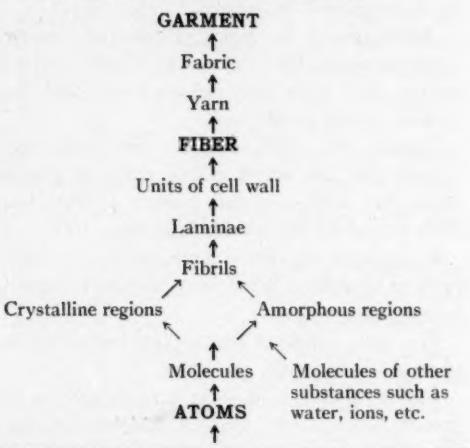
FIG. 2. *Degrees of freedom.*

modynamics to textile fibers should be viewed critically.

Energy considerations can also be applied at a finer level of structure. The consideration of the separate energies of all the molecules in a specimen would be an impossible task. Progress can only be made by using statistical methods and considering the distribution of energy among large numbers of similar particles. Energy can be associated with each of the degrees of freedom of a body. These can be worked out in simple cases (Figure 2)—for example, a diatomic molecule in a gas has seven degrees of freedom (three of translation, two of rotation, and two of vibration (K.E. and P.E. in one mode of vibration)). In a long-chain molecule the degrees of freedom are too many to be easily considered; they arise from the relative motions of all the atoms in the molecule, and from the intermolecular forces. Unless the problem can be simplified, there are severe difficulties. There are a few special cases where the results of statistical mechanics can be used in textile problems—for example, in the derivation of the relation between the dielectric constant and electrical resistance of fibers, by the consideration of the energy needed to separate ion-pairs (though in doing this, any features characteristic of fibers are eliminated by the simplifications). In general, it is not easy to apply statistical mechanics to the problems in which we are interested.

Mechanistic approach.—This approach is concerned first with structure (geometry), and then with the effect of forces on the structure. It leads to the best understanding of textiles, and explains the difficulties of the two previous approaches.

LEVELS OF STRUCTURE IN TEXTILES*



* Certain of the details of this diagram are still somewhat uncertain. The diagram is for a natural fiber—"laminae" would probably be eliminated for a synthetic fiber.

Textiles are very complex materials, and this may be ascribed largely to the number of levels at which structure occurs. These are shown in the diagram on this page.

Each level is related to the succeeding level by a particular structure. This structure will be characterized by: (*a*) volume effect—the geometry of the arrangement of neighboring elements (*e.g.*, the lattice structure in crystalline regions); (*b*) shape effect—the over-all shape which is built up (*e.g.*, the fact that we get fibers, not globular particles); (*c*) surface effect—the nature of the surface of the composite structure (*e.g.*, the particular properties of the surface layer of a fiber); (*d*) length effect—variation along the length of the structure (*e.g.*, irregularity in a yarn).

Thus, from a static point of view, we have specimens built up in a complex way, with structural arrangements at many levels, each characterized by its particular volume, shape, surface, and lengthwise properties. Effects at all the levels of structure will combine to determine the properties of the material. For example, when a force is applied, the geometrical arrangement at each level will be distorted, and the combination of all these distortions, differing in kind and degree, will determine the total change in the specimen.

As an example, we can cite some of the ways in which breakage can occur—by tearing at the seams, by loss of fabric structure as in a laddered stocking, by slippage of fibers over one another in yarn, by fiber breakage originating in the cell wall, by slippage of fibrils over one another, by slippage of molecules over one another, or by breaking the links between atoms in a molecule.

Or consider twisting. This may occur at any level due to the slippage of elements over one another, to an extent determined by the surface properties of the elements, which hold them together.

In examining any property, the behavior at any level is determined by what is happening at each of the lower levels of structure. Alternatively, one may say that the effect of any force is determined by the way the higher levels transmit it to the level under consideration. In order to solve a problem at any level, we must know (or find out): (*a*) the properties of the units, (*b*) the structure in which they are arranged, (*c*) the behavior under external influences.

We now see why textile materials are such complex substances. In a monatomic gas, for example, there is only one structural level (and that is a random arrangement) between the atoms and the volume of gas; in very few materials are there more than two or three levels. But in textiles there are six levels between atom and fiber, and three more before one gets to the finished garment.

The Importance of the Fiber

The chief problems in fundamental fiber technology today are: (*a*) understanding, leading to prediction and production, of fiber properties in terms of the molecules and their arrangements; (*b*) understanding, leading to prediction and production, of textile products in terms of fiber properties and fiber arrangement. As a corollary, there is also the problem of understanding, leading to control, of the behavior of molecules and fibers in processing.

The fiber is thus of predominant importance. This is probably because it is the lowest level of structure which can be made as a separate entity. This means that it is the lowest level on which direct experiments can be made. It also marks the division between the chemical (or agricultural) processes and the engineering processes.

Because of this predominant importance of the fiber, there is a great need for understanding of fiber properties. As a result of the complexity of fiber structure, already mentioned, this is not simple. One can take almost any simple physical quantity and write a long account of the conditions, limitations, and variations which arise when it is applied to textile fibers—this would happen with density, Young's modulus, electrical resistance, refractive index, and so on; none of these are straightforward when applied to fibers.

Expression of Fiber Properties

If one is to compare different fibers, tests must be made under comparable conditions. One difficulty in choosing the best test is the conflict between three attractions: (*a*) those properties which can most easily be related to the structure of the fiber; (*b*) those properties which can most easily be measured; (*c*) those properties which are related to the use of the fiber.

In other words, one's interest is divided between the lower levels, the level under test, and the higher levels. In practice, some compromise must be made; but the dangers of standardization on a particular set of test methods should not be forgotten. If the standardization is not related to useful properties, then one may develop fibers which are good in theory but not necessarily good in practice. Standardization may hinder real progress by directing developments into the wrong channels.

Apart from these real difficulties in the measurement of fiber properties, due to the complexity of the system and to the differing requirements, there are also difficulties in the way of expression and nomenclature. There is much truth in the view that when one gives a property a name, one is close to understanding it; although one should also remember Lord Kelvin's opinion that one does not really know anything about a property until one can express it in numbers.

The proposition of a sound terminology for the physical properties of fibers is difficult since, in most of their applications, textiles are judged by subjective impressions which are not easy to translate into precise physical terms. The difficulty is increased by the desire to use words which are easily understood—quoting de Witt Smith, "In engineering and scientific literature the true significance of this particular measure of stiffness is invariably masked for many of us under the formidable names 'modulus of elasticity' or 'Young's modulus.' I strongly urge the use of the simple, descriptive name 'elastic stiffness.' " But to many people "stiffness" does not convey the idea of resistance to extension; it conveys the idea of resistance to bending, which is the opposite of flexibility. That is the trouble with this type of term—such terms are easily understood, but they may not be understood in the right sense.

De Witt Smith also referred to strength, stiffness, and toughness (work of rupture) as important properties of fibers, and suggested adjectives to describe each of these qualities—strength going from strong to weak, stiffness from stiff to pliant, toughness from tough to yielding. This results in a glass or flax fiber being described as strong, stiff, and yielding; he realized the difficulty and said that this combination spells "brittleness." But how much better it would be merely to give figures for work of rupture, and not use any adjectives. Such adjectives as "yielding" or "brittle" fail to take account of the difference between the two stress-strain curves in Figure 3, both of which have the same work of rupture.

Another danger with easily understood words is that they have favorable or unfavorable associations. Thus, one might make the following statements about a fiber: "This fiber has good swelling recovery"; "This fiber is liable to shrink on washing." Both statements mean essentially the same thing, but one sounds good, and the other bad.

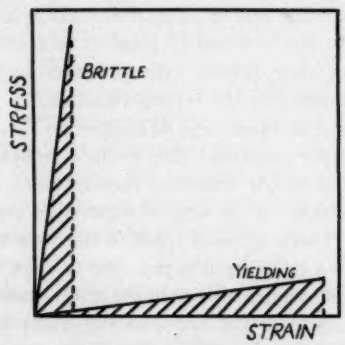


FIG. 3. *Stress-strain curves with equal work of rupture.*

For these reasons, it is better in defining the physical properties of fibers to use terms which may be rather forbidding, but which will not be distorted in meaning. There is no short cut to an understanding of the properties.

Words which are commonly understood are very useful in general description, where their complex meaning is appreciated; but if we attempt to tie this down with precise physical definitions, we not only fail to get precision, we also destroy the usefulness of the word as a means of ordinary communication—and this use is needed since textiles, in the end, are valued by their subjective impressions. We should try to define fiber properties more precisely, since it will only make for more confusion if we try to relate vaguely defined properties of final products to equally vaguely defined fiber properties.

Examples

It may help to clarify the above discussion if we consider how the ideas work out in the particular case of the mechanical properties of fibers.

Leaderman's experiments [3] on the primary creep of fibers, and Meredith's measurements [4] of stress-strain and recovery relations are both good examples of specific experiments carried out under carefully controlled conditions, eliminating as much variability of specimen as possible and making a sufficient number of tests for a reliable average to be obtained. From the results of experiments like this, the differences in behavior of different fibers can be seen and theories can be proposed. Most of our understanding of mechanical properties derives from specific experiments of this sort.

Statistical testing is well illustrated in the methods useful in the evaluation of new cottons produced by the breeder, and for comparing cottons grown in different places and different years. Here the variation in the mechanical properties between fibers in a sample must be eliminated in order to see if there is any difference between samples. This is done successfully by carrying out a very large number of single-fiber measurements in order to obtain the distribution of fiber properties; but even with the aid of such instruments as fiber sorters and magazine fiber breakers, this is a slow and expensive procedure,

and is certainly impossible for the routine examination of cotton grown by the farmer. In an attempt to overcome this, bundle tests, such as the Pressley test, have been introduced, with a sufficient number of fibers in the bundle to make the effect of variability negligible. However, this introduces the complication that the value of strength obtained depends a great deal on the coordination of fibers between the jaws. This is much affected by the way the operative prepares the sample, so that any theoretical interpretation is made difficult by the unknown effect of the form of the specimen. From a practical point of view, there is the disadvantage that there is not perfect correlation between the Pressley strength and yarn strength, so that a cotton discarded because of a low Pressley index might, if spun, have produced a good yarn. For practical evaluation, it may in fact be better to make yarn and test that, rather than rely on fiber tests.

Theoretically, one can approach the mechanical properties in the three ways described. As an example of the empirical approach, there is the Nutting-Scott-Blair equation relating stress, S, to strain, σ, and time, t, by means of three parameters, ψ, β, and κ:

$$\sigma = \psi^{-1} S^{\beta} t^{\kappa}.$$

Under carefully chosen conditions this may apply, but the specification of the conditions, or the modifications necessary for other conditions, make the treatment so complicated as to be of little value. Another way in which to express the properties is in terms of springs and dashpots. Here one uses physical models instead of mathematical equations to make an empirical approach. But in order to explain the fiber properties adequately, such a complicated collection of springs and dashpots is needed that this method does not simplify anything at all.

If the complete energy relations of the molecules and atoms were known, the mechanical properties could be predicted, but this is an impossible task. The use of simpler, generalized energy relations, such as the equations of thermodynamics, is made difficult, as discussed earlier, since one is dealing with metastable systems. For example, in simple materials, the internal energy and entropy contributions to the stress-strain relations can be separated by examining the change of stress produced by changes of temperature at constant strain. But in fibers the stress would be changing at constant strain due to stress relaxation whether or not the temperature was altered. After a long time the stress relaxation may be negligible, but, even so, one cannot be sure that this is not affected by the change of temperature. Interpretations of this type should therefore be viewed with caution, although where the difficulties are understood, the method may lead to an increased understanding of the behavior of the material. Thus, in rubber, entropy is the dominant factor (above the point of crystallization) and when free of stress the molecules are randomly oriented, so that large extension can be obtained by applying a force to straighten them; as soon as the force is removed, the molecules become disorderly, the entropy increasing. But in fibers, internal energy forces are strong enough to keep the molecules oriented and to give the properties needed in a fiber. Entropy effects will be secondary, but may be important in some aspects of fiber behavior—for example, the recovery behavior.

The clearest picture of mechanical properties comes from a consideration of what is happening to the molecular arrangement—that is, by the mechanistic approach. For example, a typical fiber stress-strain curve consists of three regions. First there is a region of high modulus, resisting extension strongly and giving a recoverable extension; this is due to a stretching of interatomic bonds and intermolecular cross-links, which requires a fairly large force; as soon as it is removed, the links retract to their original position. When the cross-links become strained beyond a certain amount, they break, and this allows a considerable molecular movement, resulting in a large extension for a small increase of force—this is the second region of the curve. When the force is removed, the cross-links may not be re-formed in the same places, and so the extension will not be completely recovered. As more cross-links break, the molecules become better aligned, and it becomes increasingly difficult to get further extension by aligning them better—this gives the third region of the curve, which has a steeper slope. Finally, break occurs, due either to breakage of molecules or to slippage of molecules over one another, depending on the length of the molecules. Many other mechanical effects—*e.g.*, the difference between different fibers, the influence of moisture and of time, torsional behavior, and crease-resistance—can be explained by similar arguments, demonstrating the advantages of the mechanistic approach.

Conclusion

This paper puts forward a personal viewpoint on the scientific approach to problems in textile technology. Many will disagree with some of the opinions expressed, but criticism and discussion will be valuable in promoting a better understanding of the subject. A sound physical approach is necessary in solving the problems of relating the properties required in final products, whether fibers or fabrics, to the factors which cause them. This is a problem which is important not only to the physicist interested in fibers, but to the whole textile industry, and to the producers and users of fibers. It is most important that there should be discussion of the general problem leading to education in the industry, and to demolition of cranky ideas among the scientists.

Because of the complexity of textile fibers, due to the many levels of structure, the problems will never be simple ones. And also because of the complexity, and the number of factors involved, not all of which can be controlled, the physicist must have a broader view than is necessary in some more precise parts of physics; and he may, with advantage, learn something from other ways of thought, such as those used in biology or in technology.

Literature Cited

1. de Witt Smith, H., *Am. Soc. Testing Materials, Proc.* **44**, 543 (1944).
2. Balls, W. L., "Studies of Quality in Cotton," London, Macmillan and Co., Ltd., 1928, p. 316.
3. Leaderman, H., "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," Washington, D. C., The Textile Foundation, 1943.
4. Meredith, R., *J. Textile Inst.* **36**, T107, T147 (1945).

(*Manuscript received June 4, 1953.*)

Device for the Rapid Determination of Tangents to Stress-Relaxation Curves of Single Wool Fibers

W. J. Thorsen

Western Regional Research Laboratory, Albany, California*

INCREASING ATTENTION has recently been given to the stress-relaxation properties of single fibers. Studies of these properties in wool and mohair fibers have been carried on at this laboratory with the aid of a sensitive strain gage (to be described in a later publication) and a single and multiple point recorder. The initial stress relaxation (from 2 to 600 sec.) is recorded on the single point recorder, and the forces at longer times are recorded on the multiple point recorder. The rate of change of the force with time or the tangent to the curve at various times is one of the measurements taken, but it has been found that the usual procedure for determining these tangents is quite tedious, especially since large numbers of readings are required. The usual procedure is to estimate the angle of the tangent with a protractor reading in degrees, and then to look up the value of the tangent in the tables. In a recent description † of a tangent-measuring instrument, seven steps are required to obtain the value of a tangent to a curve.

A considerable saving in time is achieved by the expedient of calibrating the protractor to read the value of a tangent directly. We wish to suggest how one may construct such an instrument and how it may be used to advantage.

The tangentometer shown in Figure 1 is made of $\frac{1}{16}$-in. transparent plastic in the shape of a quadrant with one side extended. In Figure 2 it is shown placed on the strip-chart recording of a wool stress-relaxation curve *OP* for a measurement.

Portion *ABC* is the quadrant with its center, *A*, at

* Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

† J. F. Waters, *J. Sci. Instruments* **28**, 116 (1951).

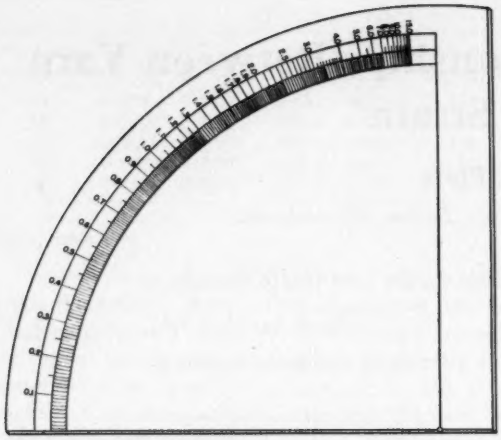


FIG. 1. *Tangentometer. The scale reads directly in tangents.*

straight edge *BAE*. The extension *AECD* has the purpose of extending side *BA* to *E* to permit more accurate alignment of the tangentometer side *BE* with the true tangent of the curve *OP* at the point being measured. A small notch is located at *A* to facilitate alignment of line *CA* with the point to be measured. A prism may be used at *A*, but is not recommended in the case where there is any jaggedness of the curves, as in records obtained frequently from recording potentiometers. The radius *BA* is 16.5 cm. in length, and extension *AE* 2.0 cm. The values of the tangents may be scribed on the tangentometer with the aid of a drafting machine. The following ranges in calibration, slightly different from those on the prototype shown in Figures 1 and 2, are recommended for convenience in reading: (*a*) 0.01-unit steps up to 1.3, (*b*) 0.02 unit apart to 3.0, (*c*) 0.1 apart to 6.0, (*d*) 0.2 apart to 10.0, (*e*) 0.5 apart to 13, and (*f*) 1.0 apart to 15. Slopes greater than 15 are not generally required, and may or may not be scribed on the protractor. Zero slope is registered at *B*, and infinite slope would be registered at *C* if the scale were completely scribed.

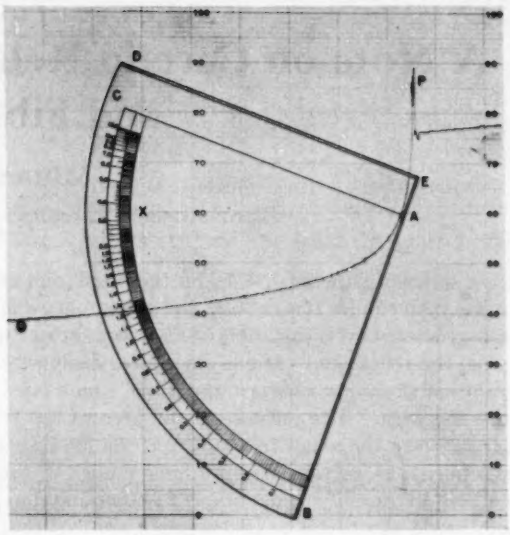


FIG. 2. *Tangentometer applied to a strip chart record of stress-relaxation.*

The measurement of slopes along a curve is facilitated by readings at the points of intersection of the curve with the horizontal coordinates of strip-chart records or may be drawn in through selected points to be measured. The tangentometer is placed with *A* over the point to be measured and with side *BAE* tangent to the curve at that point. The tangent is then read off directly on the scribed scale at *X* (see Figure 2).

The tangentometer will read both positive and negative slopes, and is inverted when going from positive to negative slopes.

(*Manuscript received August 25, 1953.*)

A Note on Certain Relationships Between Yarn and Fiber Strain*

Milton M. Platt

Fabric Research Laboratories, Inc., Boston, Massachusetts

IN a series of papers [3, 4, 5] on the mechanics of singles yarns under tensile load and the influence of yarn geometry on translation of fiber strength into yarns, the writer and various coworkers dealt with strain distributions amongst the fibers which comprise the yarn. The purpose of the present report is to indicate the magnitude of the errors in strains consequent to certain assumptions made in the analyses to simplify the work. The two assumptions made which will be investigated are: (*a*) that the effects of helix angle changes are negligible; and (*b*) that lateral yarn contraction effects are small. It will be shown herein that within the practical range of yarn twists—*i.e.*, yarn surface helix angles less than 30°—both assumptions are reasonable. The need for this clarification was made evident to the writer in a current research on the relationships between the strength of plied yarns and the mechanical properties of their constituent singles yarns.

Strain distributions in twisted singles yarns have been shown to be calculable from

$$e_f = e_y \cos^2\theta_o, \tag{1}$$

where e_f is the fiber axial tensile strain resulting from a yarn tensile strain e_y, and θ_o is the helix angle between fiber and yarn axes. Equation (1) was derived from a geometric analysis of the deformed helix, assuming small changes in helix angle concomitant with the yarn strain e_y, and also negligible change in helix radius—*i.e.*, Poisson's ratio of zero.

That the first of these assumptions—that of negligible effect of helix angle changes—is valid for most textile yarns can readily be seen from the results of a more rigorous analysis, as follows:

Let a = helix radius, N_o = number of turns of twist per unit length prior to yarn strain imposition, and L_{yo} = original yarn length. Then, for a yarn strain e_y, the yarn length changes to

$$L_{y1} = L_{yo}\,(1 + e_y). \tag{2}$$

The yarn twist similarly changes to

$$N_1 = \frac{N_o}{1 + e_y}. \tag{3}$$

Since the fiber path is helical before and after yarn straining, the fiber lengths for the two cases can be seen to be:

$$L_{fo} = \frac{L_{yo}}{\cos\theta_o} = L_{yo}\sqrt{1 + 4\pi^2 N_o^2 a^2};$$

$$L_{f1} = \frac{L_{y1}}{\cos\theta_1} = L_{y1}\sqrt{1 + 4\pi^2 N_1^2 a^2}. \tag{4}$$

The axial fiber strain e_f is then

$$e_f = \frac{L_{f1} - L_{fo}}{L_{fo}} = \frac{L_{f1}}{L_{fo}} - 1$$

$$= \frac{L_{y1}}{L_{yo}}\sqrt{\frac{1 + 4\pi^2 N_1^2 a^2}{1 + 4\pi^2 N_o^2 a^2}} - 1. \tag{5}$$

Following substitution of equations (2) and (3), equation (5) may be rewritten as

$$e_f = (1 + e_y)\sqrt{\frac{1 + \dfrac{4\pi^2 N_o^2 a^2}{(1 + e_y)^2}}{1 + 4\pi^2 N_o^2 a^2}} - 1, \tag{6}$$

which becomes, after simplification,

$$e_f = \sqrt{\frac{(1 + e_y)^2 + 4\pi^2 N_o^2 a^2}{1 + 4\pi^2 N_o^2 a^2}} - 1. \tag{7}$$

Assuming $e_y \ll 1$, equation (7) can be simplified further to

$$e_f = \sqrt{\frac{1 + 4\pi^2 N_o^2 a^2 + 2e_y}{1 + 4\pi^2 N_o^2 a^2}} - 1$$

$$= \sqrt{1 + 2e_y \cos^2\theta_o} - 1. \tag{8}$$

Assuming $2e_y \cos^2\theta_o \ll 1$, then from binomial expansion of the square-root term of equation (8),

* Part of a project supported by the Office of Naval Research.

TABLE I. FIBER STRAINS, e_f, FOR VARIOUS YARN STRAINS

Yarn helix angle, θ_o	$e_y = 0.020$		$e_y = 0.100$		$e_y = 0.200$		$e_y = 0.300$		$e_y = 0.500$		$e_y = 1.00$	
	Eq. (9)	Eq. (7)	Eq. (9)	Eq. (7)	Eq. (9)	Eq. (7)	Eq. (9)	Eq. (7)	Eq. (9)	Eq. (7)	Eq. (9)	Eq. (7)
0°	0.0200	0.0200	0.100	0.100	0.200	0.200	0.300	0.300	0.500	0.500	1.000	1.000
10°	0.0194	0.0194	0.097	0.097	0.194	0.195	0.291	0.292	0.484	0.486	0.970	0.980
20°	0.0176	0.0176	0.088	0.089	0.177	0.179	0.265	0.269	0.442	0.454	0.884	0.910
30°	0.0150	0.0150	0.075	0.075	0.150	0.154	0.225	0.232	0.375	0.392	0.750	0.801
45°	0.0100	0.0100	0.050	0.051	0.100	0.104	0.150	0.160	0.250	0.271	0.500	0.585

there results

$$e_f = e_y \cos^2\theta_o. \tag{9}$$

Thus, the validity of the previous analysis derived graphically is analytically shown to be more dependent upon the existence of small strains in the structure than upon the magnitude of the helix angles. Calculations from equations (9) and (7) yield the results shown in Table I. As can be seen from Table I, the errors produced by using the approximate formula (9) are in most cases negligible. The rigorously computed strains are higher than those given by equation (9), as would be anticipated from the fact that positive terms were neglected in the replacement of equation (7) by equation (8). For helix angles below 45° equation (9) is a sufficiently precise representation of the strains given by equation (7) for practical use in analysis.

It is interesting to note that in the analysis of fiber strains produced by yarn bending, Backer [1] showed that if no freedom of fiber relative motion exists, local fiber strain may be represented by the following equation:

$$e = \sqrt{\frac{\left(\frac{r}{a} - \cos\varphi\right)^2 + \lambda^2}{\left(\frac{r}{a}\right)^2 + \lambda^2}} - 1, \tag{10}$$

where e is the local fiber strain, a is the helix radius of the fiber, r is the radius of curvature of the center line of the bent yarns, φ is the parametric angle which locates the fiber in the yarn cross section, and $\lambda = (r/a)\tan\theta_o$ is a convenient dimensionless parameter which physically is a measure of the ratio of turns of twist of the yarn to curvature of the yarn axis created by bending. The angle φ is such that y, the distance of any fiber from the yarn neutral axis, is

$$y = -a\cos\varphi. \tag{11}$$

From elementary bending considerations, the local yarn strain, e_y, would be determined from

$$e_y = \frac{y}{r} = -\frac{a\cos\varphi}{r}. \tag{12}$$

Thus, equation (10) may be rewritten as

$$e = \sqrt{\frac{\left(1 - \frac{a}{r}\cos\varphi\right)^2 + \tan^2\theta_o}{1 + \tan^2\theta_o}} - 1$$

$$= \sqrt{\frac{(1 + e_y)^2 + \tan^2\theta_o}{1 + \tan^2\theta_o}} - 1. \tag{13}$$

Inspection of equations (7) and (13) indicate them to be identical. Clearly, then, local strains produced by bending, as given by equation (10), are a manifestation of changes in helical path length, and thus equation (9) may be used as a close approximation for such local fiber strains. That is, for bending, with no freedom of motion, the fiber strain may be determined from

$$e = e_y \cos^2\theta_o$$

$$= \frac{y}{r}\cos^2\theta_o. \tag{14}$$

Equation (14) was used in a discussion of strains produced by bending involved in fabric creasing [2], assuming no freedom of relative fiber motion, and it is clear that its use is justified whenever $e_y = y/r$ is small compared to unity. Even in the case of a yarn bent about itself—*i.e.*, $y/r = 1$—the approximate formula gives, for $\theta_o = 45°$, 50% strain, while the more precise equation (13) gives 58.5%. The more realistic case of $y/r = \frac{1}{2}$—*i.e.*, where yarns are bent about each other—would give, for $\theta = 45°$, an approximate result of 25% compared to the more precise value of 27.1%. For helical angles smaller than 45°, smaller discrepancies result—*e.g.*, for $\theta_o = 30°$ and $y/r = 1$, the approximate value of $e = 75\%$ should be compared with 80% obtained from equation (13).

In addition to the effects of helix angle changes on strain, consideration should also be given to the effects of changes in helix radius, for both yarn tension and bending. The writer indicated an approach to this problem in an early paper [3] on strains in continuous-filament yarns, wherein it was shown that for a constant volume stretch—

i.e., a Poisson's ratio for the yarn of approximately ½—fiber tensile strains, e_f, produced by a yarn tensile strain, e_y, could be determined from

$$e_f = \frac{1}{(1 + e_y)^{\frac{1}{2}}} \sqrt{\frac{(1 + e_y)^2 + \tan^2\theta_o}{1 + \tan^2\theta_o}} - 1. \quad (15)$$

Note that lateral *forces* were not considered in the development of equation (15). Again, assuming $e_y \ll 1$, equation (15) reduces to

$$e_f = \frac{e_y}{2} (3 \cos^2\theta_o - 1). \quad (16)$$

It would intuitively be predicted that lateral yarn contraction will reduce fiber tensile strains for a given yarn tensile strain. The extreme physical case of no lateral resistance—*e.g.*, collapse of the yarn cross section—will indicate that there may be yarn strains with zero concomitant fiber axial tensile strain. Comparison of equation (16) with equation (9) will indicate that for a constant volume yarn stretch, fiber strains are less than those given by equation (9), the differences increasing with increases in yarn helix angle. For a 25° helix angle, differences of less than 10% exist between the results of equations (9) and (16). For an angle of 30°, which the writer considers to be the practical limit for the validity of the assumption of helical paths with no fiber buckling, differences in strain of 15% exist between equation (16) and equation (9)—*i.e.*, for a yarn strain of 2%, equation (9) would predict a 30° helix angle fiber to bear a strain of 1.5%, while equation (16) would give 1.3%. For higher yarn strains, say 20%, equation (9) would give a fiber strain of 15% for a 30° helix angle fiber, equation (16) would give 12.5%, and equation (15) would give 13.6%. For high-elongation fibers, smaller discrepancies would be introduced by replacing equation (15) by equation (9) than for low-elongation fibers. It is probably closer to reality to assume constant-volume distortion for highly extensible fibers, while low-extensibility fibers would probably exhibit lateral contractions consistent with a lower Poisson's ratio than ½. If this is true, then, in the practical case, equation (9) would always give usable results.

As concerns yarn strength, it should be noted that lower fiber strains resulting from the higher helix angle of the fibers will produce decreased fiber strength translation. A greater strain variance will exist amongst the fibers if helix radii decrease in accordance with a constant volume distortion than that given by equation (9). The effect on strength will be greatest for low-elongation, high-modulus fibers. In terms of the nomenclature previously used by the writer, lateral contraction will change the "serigraph" effect, but the component effect will be unaltered. When averaged over the entire yarn cross section, differences in strain and hence stresses less than those given in the example above will occur, since not all fibers have the same helix angle. Since the component effect is unchanged, only one of the factors which decrease translation of fiber strength will be affected by lateral contraction. Thus, the existence of lower external fiber strains, and hence lower stresses, than those given by equation (9) will have the same effect on strength translation as a decreased a/b. Such an effect has been shown to be small [5] for a yarn containing fibers with any appreciable variability in extension to break, which is usually the case of low-extensibility fibers. For uniform fibers having a rupture elongation 2% and an a/b of 0.0, calculations indicate the effect of constant volume stretch on strength to be about 7% for a 30° helix angle yarn. For the same parameters, but with a variation of fiber elongation to break of 10%, the effect on strength is reduced to less than 3%.

Considering that a constant volume distortion is probably extreme, it appears that lateral contraction plays a secondary part in the over-all efficiency of strength translation of fibers into yarns for helix angles less than 30°. The magnitude of the effect would have to be determined by extremely precise experiments, in light of the small magnitude theoretically indicated. Obviously, yarns whose helix angles exceed 30° may suffer significantly in strength as a result of any lateral yarn contraction. For such cases, the experimental determination of the effective Poisson's ratio would be required in order that yarn strength calculations be made.

Literature Cited

1. Backer, S., TEXTILE RESEARCH JOURNAL **22**, 668 (1952).
2. Hamburger, W. J., Platt, M. M., and Morgan, H. M., TEXTILE RESEARCH JOURNAL **22**, 695 (1952).
3. Platt, M. M., TEXTILE RESEARCH JOURNAL **20**, 1 (1950).
4. Platt, M. M., TEXTILE RESEARCH JOURNAL **20**, 519 (1950).
5. Platt, M. M., Klein, W. G., and Hamburger, W. J., TEXTILE RESEARCH JOURNAL **22**, 641 (1952).

(*Manuscript received November 23, 1953.*)

Studies on the Soluble Proteins of the Silk Gland of the Silkworm, *Bombyx mori*

E. H. Mercer*

Contribution from Textile Research Institute, Princeton, New Jersey

Abstract

The precursors of silk fibroin were extracted in sodium bicarbonate solution from the silk gland of the silkworm, *Bombyx mori*, and studied by ultracentrifugation. Three components ($s \sim 1.8$, 1.5, and 1) were found, but there was insufficient evidence to show whether these were three different proteins, aggregates, or configurational variants. In solutions containing urea, only one component was detected.

On standing, the viscosity increased and a fibrous gel formed. During this change the sedimentation velocities decreased and the polydispersity increased. The mechanism of this change is discussed.

The gland extract initially gave a silk *I* type x-ray pattern and after aging a silk *II* pattern. The other constituents of the fiber—sericin, pigments, and waxes—were also present in the gland. In the storage vessel the sericin surrounded the fibroin.

Introduction

The silk glands of the mature silkworm (*Bombyx mori*) contain a viscous yellow solution which, on extrusion from the spinnerets near the mouth of the worm, is transformed into silk. Just prior to spinning, the two glands may contain in all about 0.5 g. of protein which, as was shown by Foà [6], is in a form that is readily soluble in aqueous solutions. This viscous solution is in an unstable state, and is changed readily into the condensed insoluble fibrous form by stretching the gland [16]. Aqueous extracts are likewise unstable and, depending on their protein concentration, may slowly coagulate to a gel or deposit a fibrous precipitate. Because of the economic importance of silk, many investigators have been interested in the mechanism of the transformation from the soluble precursor into the insoluble fiber. This earlier work was reviewed by Bergmann [1] and need not be described here.

The silk thread of the cocoon spun by the silkworm consists of two proteins, sericin and fibroin, both produced from the silk gland. It is therefore desirable to determine the state of these two substances in the silk gland and the way in which they separate and reach their final location in the extruded thread. It was once thought that sericin was a modified surface layer of fibroin, and this view was revived recently by Happey and Hyde [7]. The two proteins have also been thought to exist mixed in solution in the gland. Meyer and Jeanerat [17], having in mind the very concentrated solution (30% of protein), thought the two proteins might somehow stabilize each other in solution. The histological work of Yamanouchi [24] showed, however, that, contrary to these views, the two proteins are quite distinct from the time of their first appearance in the secreting cells which line the gland, and that in the storage vessel (middle section) of the gland the fibroin has collected together to form a core with the sericin already enveloping it. As the two proteins travel down the tapering exit tubule towards the spinnerets, the separation persists and prevails in the extruded fiber. These conclusions were fully confirmed in the present work, and made the basis of methods for separating samples of sericin and fibroin from the gland.

It is important for the consideration of the results of the sedimentation analysis (to be described in the experimental section) to find out whether any sericin is dissolved when the excised gland is extracted, with sodium bicarbonate solution used as a solvent. Foà [6] many years ago reported that only the fibroin precursor was extracted by aqueous solutions. Meyer and Jeanerat [17], using a strongly alkaline solution, concluded that both proteins could be extracted. Therefore, various experiments of a histological and histochemical nature, ancillary to the major investigation, were carried out to clarify these points, and these will be described first.

* Former Visiting Fellow, Textile Research Institute.

Experimental

The silkworms used in this study were raised from eggs obtained from the General Biological Supply House, Chicago, Ill. No special precautions were observed during their development.

Microscopy

Mature worms were fixed whole in formol saline, and after some weeks the spinning apparatus was removed intact by dissection under water. The three sections of the glands—the long convoluted secretory tube, *S*, which ends blindly, the storage vessel, *M*, and the tapering exit tubule, *T*—are readily distinguished in worms of this stage, as may be seen in the photograph of Figure 1. Cross sections were cut from each of the three zones and stained by procedures similar to those of Yamanouchi [24]. The sections of the storage vessel (middle section, *M*, of Figure 1) and the exit tubule, *T*, showed the fibroin core and the sericin surrounding it. The boundary between the two protein solutions was quite sharply defined. Fibroin alone appeared to be present in the secretory tubules. These findings agree with those of Yamanouchi.

Glands fixed in formalin were dehydrated in an alcohol series, mounted in toluene, and examined by means of a polarizing microscope. The fibroin core and sericin annulus were readily distinguished between crossed polaroids. No well-defined double refraction was exhibited by the fibroin core of the storage vessel. Orientation appeared in the tapering exit tube, but the double refraction remained below that of the extruded fiber. The annulus of sericin surrounding the fibroin core of the storage vessel exhibited double refraction when viewed in cross sections or in longitudinal sections, but not when viewed in a direction perpendicular to the surface of the gland. These optical properties are summarized in Figure 2. The same type of optics is shown by the sericin layer of the cocoon silk, as reported by Ohara [18] and by Simizu [20], and is evidence that the sericin has fibrous characteristics even in the gland and that its

FIG. 1. *Photograph of silk gland of* Bombyx mori *(fixed in formol saline and photographed by reflected light). T is the exit tubule leading to the spinneret in the mouth of the worm, M is the storage vessel, and S is the secretory portion of the gland. In the storage vessel the fibroin core with the wrinkled surface is readily distinguished from the sericin annulus.*

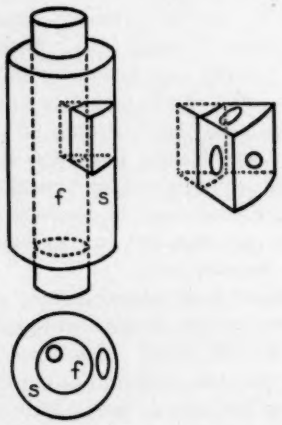


FIG. 2. *Optical properties of the storage vessel of the silk gland. A short length of the fibroin core,* f, *is shown encircled by the sericin annulus,* s *(drawn relatively thicker than found, for purposes of emphasis). The optical properties noted in various sections are indicated by the conventional symbols:* o = *isotropic;* 0 = *anisotropic.*

orientation is less affected by extrusion than is that of the fibroin.

Separation of the Two Secretions

Further evidence of the definite separation of the two proteins in the middle section of the gland was obtained from glands which had been fixed in alcohol solutions. Freshly removed glands were placed in 25% ethanol for 4 to 8 hrs. Both protein solutions coagulated, and the yellow sericin layer could be peeled away by hand from the hardened fibroin core. The fibroin had become quite brittle, whereas the sericin retained some pliability and could be stretched to between two and three times its length. The surface of separation between the two proteins was quite distinct, in spite of the fact that in the central part of the storage vessel it was thrown into ridges, as can be seen in the photograph (Figure 1). In formalin-fixed material it was not found possible to separate the two proteins in this way, presumably owing to a cross-linking of the two layers.

The extraction of the freshly removed gland by sodium bicarbonate solution was studied directly by means of a low-power microscope. Short lengths (2 to 5 mm.) were cut from the middle section of freshly removed glands and placed in a 1% sodium bicarbonate solution. The pale yellow solution from the core of the vessel was observed to swell and well out from the cut ends and to pass into solution. The more deeply pigmented layer of sericin adjacent to the enveloping cellular wall of the gland grew more opaque in appearance and did not dissolve, but remained as a hollow tube after the fibroin core had been extracted. This residue was removed, washed, stretched, dried, and submitted to x-ray examination [14]. Spacings characteristic of sericin and of waxes and fats were found in the x-ray pattern. These observations are not finally satisfying as proof that no sericin is extracted, but it seems that the amount entering solution is small.

When glands were extracted with 5% ammonia solution, some sericin was observed to dissolve, giving a stronger yellow color to the solution. This result is in agreement with that of Meyer and Jeanerat.

Preparation of Aqueous Extracts of the Silk Glands for Ultracentrifugation

Silk glands were removed from worms toward the end of the fifth instar after they had ceased eating and showed an inclination to begin spinning. It was hoped that all such worms would be in a similar physiological condition. The excised glands were washed briefly in distilled water and placed in a solution of 1 g. of sodium bicarbonate in 100 ml. of water. In the bicarbonate solution the storage vessels of the glands swelled and burst, and a portion of their contents passed into solution.

The pale yellow viscous extract was filtered through a coarse mesh filter and centrifuged at 3,000 r.p.m. for 15 min. This extract formed the basis of other preparations. Usually sufficient protein was extracted to give a protein concentration of 1% to 2% (found by drying an aliquot at 50°C).

Such solutions are faintly turbid and viscous. During a period of some hours to several days, the turbidity and viscosity increase and the solution finally sets to a gel. Meyer and Jeanerat, using a more alkaline extract than the above, measured the marked increase in viscosity which occurs during this change. The relative viscosity increased from 2.2 to 3.32 in 18 hrs.

One of the most interesting properties of these solutions is the ease with which the soluble proteins can be separated as fibrous strands by shaking. These fibrillar strands are strongly coherent and birefringent. Examination in the light microscope, followed by the electron microscope, revealed that they consist of fine fibrils clumped together in roughly parallelized bundles [13]. When solutions are allowed to stand without disturbance for some days, they grow more turbid and viscous, and the tendency to produce fibrillar strands on shaking is much enhanced. This change will be referred to as "aging." A solution which has aged for several days deposits fibrils or may even gel when stirred. Gentle centrifugation (3,000 r.p.m. for 1 min.) of solutions a few days old was found to cause the progressive separation of well-parallelized tufts of fibrils at the surface. Birefringence measurements on the most densely coherent of these bundles gave values of the order of 0.03—*i.e.*, about two thirds that of silk fiber spun in the normal way.

The gels produced on standing were usually found to be isotropic, but on several occasions optical anisotropy developed spontaneously, possibly as a consequence of orientation initiated by earlier disturbances.

The extracted protein was readily precipitated from solution by the addition of acids, of alcohol, or of strong salt solutions. The precipitates were white, strongly coherent, and sticky, and could be drawn by

hand into well-oriented threads which on drying became rather brittle. These fibroin precipitates bear a resemblance to chewing gum, and it is interesting to note that this property is also possessed by fiber-forming precipitates of regenerated wool keratin [12, 19] and feather keratin [11]. The oriented threads were birefringent, and yielded good fiber type x-ray patterns identical with that of fibroin spun by the worm.

Sedimentation Analysis

A Spinco ultracentrifuge was used, and all runs were made at 59,780 r.p.m. in a 12-mm. cell. The buffer solution was 1% sodium carbonate, and the pH of the protein solution was between 8 and 8.3. The principal subjects investigated were: (*a*) the composition of the fresh extract, and (*b*) the changes produced by aging and shaking.

The course of a typical sedimentation run using a freshly made solution is shown in Figure 3. Three main components were invariably found, and will be referred to as α, β, and γ in order of decreasing velocity of sedimentation. The solutions even when fresh were slightly turbid, and part of this turbidity persisted even after a preliminary sedimentation of 20,000 r.p.m. for 20 min. The material causing this turbidity was removed from solution during the period of acceleration in the ultracentrifuge. In many of the runs a small amount of a slow-moving component (δ) was also present.

TABLE I. SEDIMENTATION CONSTANTS OF THE THREE MAJOR COMPONENTS OF FRESH EXTRACTS OF THE SILK GLAND *

α	β	γ
1.6	1.2	0.9
1.8	1.4	1.1
1.9	1.6	1.2
1.8	1.7	1.5
2.1	1.8	1.5

* An average value has not been calculated because there seem to be substantial differences between the behavior of the several extracts.

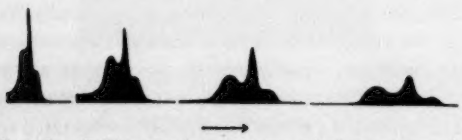


FIG. 3. *Sedimentation patterns of the extract of the silk gland in 1% sodium bicarbonate solution. The meniscus is at the left. Exposures were made at 20, 40, 60, 80 min. after reaching speed.*

Silk cocoons are always more or less colored with a yellow pigment associated mainly with the sericin, as may be seen either by an examination of the silk threads or of cross sections of the storage vessel of the gland. The fibroin also has a slight yellow color and its solutions from the gland are similarly colored. During sedimentation it was noted that the color sedimented with the protein, leaving a clear supernatant. The pigments therefore seem to be associated directly with the protein.

Total protein concentration was calculated from the area under the sedimentation curves, using an expression given by Svedberg and Pedersen [21], and was compared with that found by drying and weighing the residue from a measured volume of solution. The agreement was satisfactory. The better sedimentation curves were analyzed into their separate components. Sedimentation constants were then calculated from the positions of the constructed peaks at 30 and 60 min. These were reduced to standard conditions, and are tabulated in Table I.

The appearances of the three peaks (α, β, and γ) in *fresh* extracts (see Figures 3 and 4) are worth noting. Usually the central peak (β) is relatively sharper and narrower; the fastest and slowest peaks (α and γ) have a more normal aspect. In general, the spread of a peak during sedimentation may be due to diffusion or polydispersity or both. A very sharp peak showing little spread may mean a very small diffusion constant—*i.e.*, possibly a very asym-

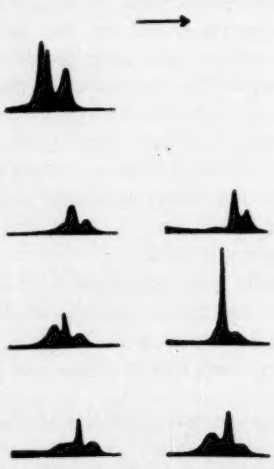


FIG. 4. *Sedimentation patterns of different batches of worms. Three components are always present, but the relative concentration and other characteristics are not the same.*

metric molecule. Therefore, in order to obtain a better characterization of the three peaks found here, apparent diffusion constants (D_A) were calculated, assuming the observed spread to be due to diffusion alone.

The results of these calculations have no great claim to accuracy, but they do show that component β in fresh extracts may have an extremely small apparent diffusion constant ($< 0.5 \times 10^{-7}$ cm.^{2} sec.$^{-1}$) for a molecule with sedimentation constant of the order of 2*s*. The α and γ peaks yielded values more nearly of the same order as proteins having similar *s* values. A further puzzling observation is immediately apparent from an inspection of Figure 4, which shows a series of sedimentation curves obtained from extracts made from different batches of worms. It is obvious that strikingly different patterns are given by different preparations, and presumably this may mean that the compositions of the secretions of the individual worms are different, although all of the worms studied here were at the same stage of development, as judged by their behavior. Three peaks are always present, but the relative proportions of the three components and the appearances of their peaks differ. These differences are borne out by further analysis of the sedimentation curves. Table II shows in particular the relative proportions of the three components, as calculated from the analysis of several of the better curves. The figures show that component γ (slowest) is present in the greatest concentration.

TABLE II. CONCENTRATIONS OF THE THREE COMPONENTS IN SILK GLAND EXTRACT COMPUTED FROM AN ANALYSIS OF THE BETTER-DEFINED SEDIMENTATION CURVES

α (%)	β (%)	γ (%)
14	31	55
23	26	51
26	27	47
37	29	44
33	32	35

TABLE III. EFFECT OF AGING ON SEDIMENTATION CONSTANTS

Peak	Original *s* value	*s* Values in aged solution	Time of aging
α	1.6	1.3	9 days
β	1.2	0.8	9 days
γ	0.9	0.5	9 days
α	1.8	1.4	23 hrs.
β	1.4	1.0	23 hrs.
γ	1.1	0.7	23 hrs.
α	1.9	1.8	20 hrs.
β	1.6	0.8	20 hrs.
γ	1.2	0.4	20 hrs.
α	2.1	1.3	shaken
β	1.8	1.0	shaken
γ	1.5	0.3	shaken

An extract made with distilled water only (with 0.1*M* sodium chloride added just prior to centrifugation) gave a similar curve.

The effect of aging and shaking.—Extracts were allowed to stand at room temperature (22°C) for several hours or in a refrigerator at 5°C for periods up to 2 weeks. At intervals aliquots were withdrawn and examined in the ultracentrifuge with the object of following the changes which led to gelation. The entire experiment could not be carried out on a single preparation, but observations on several extracts at various times were made to cover the range. The effect of aging on the sedimentation pattern was very striking. With increasing time of aging (1 day to 2 weeks) each component sediments more and more slowly and each peak grows progressively broader, until just prior to gelation the rates of sedimentation may have dropped to one half of the original rates and the three peaks may have merged to such a degree owing to their spread that their separation by analysis of the composite curve is scarcely possible (Figure 5 and Table III).

Calculations (based on apparent diffusion constants) show that the broadening of the peaks could not now be due to diffusion alone, since this would imply impossibly large diffusion constants. It is necessary to conclude that polydispersity has developed in each of the three components. The increase in poly-

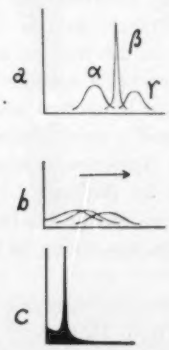


FIG. 5. *Comparison of sedimentation curves of* (a) *fresh and* (b) *aged extracts to show modification in shape of individual curves (the composite curves have been analyzed into their separate components)*; (c) *shows the single peak in strong urea solution (1 hr).*

dispersity was progressive, and in respect of this change each of the molecular species behaved in the same general way irrespective of the original shape of its peak. Different preparations changed at different rates, and this agrees with the observation (first made by Foà) that different preparations gel at different rates. In the present series of experiments it was noted that the treatment of the solution, the concentration, the degree to which it was initially centrifuged, and more obscure factors influence the time of gelation.

Sericin solutions.—A sample of sericin was extracted from freshly spun cocoons by warming these with sodium bicarbonate (pH 8.3) at 40°C for 12 hrs. Such an extract probably contains what has been referred to as "sericin *A*." It was examined in the ultracentrifuge to compare its behavior with that of the gland extract, as an aid in the identification of the gland constituents. The rate of sedimentation was very low (indicating an s value < 0.5) and the peak was broad and ill-defined.

Effect of protein concentration on sedimentation constants.—Sedimentation runs were made at three different protein concentrations to determine whether there was a dependence of sedimentation constant on concentration. A fresh extract was prepared with a protein concentration of 1.4%, and this was diluted by the addition of 1% sodium bicarbonate solution to give concentrations of one half and one third of this. A lower concentration, although most desirable to facilitate an extrapolation to zero concentration, was not practicable owing to the inadequacy of the optical system of the instrument.

An unsatisfactory feature of the experiment, which was realized in advance, was the fact that it took 2 days to complete. In this time, as earlier experiments had shown, there occurs a spontaneous change in the solutions leading to a marked slowing of the rate of sedimentation and a modification in the shape of the curves. This change was superimposed on the changes produced by dilution. The more concentrated solutions were run first, which means that the most dilute solution was about 24 hrs. old when examined.

The results showed an *increase* in rates of sedimentation, on diluting from 1%to 0.6%, of between 25% and 50% of the original rate of sedimentation. When account is taken of the slowing down due to aging, which must have occurred, this suggests a considerable dependence of s on concentration.

Effect of high pH and of urea.—The pH of a bicarbonate extract was raised to 10.3 by the addition of drops of concentrated ammonia immediately prior to centrifugation. The sedimentation curve was greatly modified. A single sharp peak separating into two toward the end of the run was observed. The same solution after standing for 3 days showed a broadening of the peak, and the solution gelled after 6 days.

The addition of urea also produced a remarkable change. Solid urea was added to a bicarbonate extract to give a urea concentration of 5*M*. A single, very sharp, slowly moving peak was observed in this solution. The extract did not gel, and, although fibers could be formed by vigorous shaking, the urea obviously interfered with this reaction.

Electrophoresis, diffusion, and light scattering.—Difficulties were encountered in attempting electrophoresis, owing to the tendency for all surfaces to become coated with a thin fibrous film. Almost invariably this property prevented the formation of satisfactory boundaries. Only in one instance was a good boundary formed and an experiment attempted. In a buffer of pH 8 two components and possibly a third were separated in a 3-hr. run. The same difficulties prevented an attempt to determine an average diffusion coefficient. Diffusion experiments would also be complicated by the changes due to aging which would become apparent in the time required to carry out such an experiment.

It is clear that experiments of this character are only possible with solutions stabilized by chemical modification of the proteins, and experiments on these lines are planned.

An examination of extracts in sodium bicarbonate solution by means of light scattering has been carried out by Mr. P. C. Colodny (Textile Research Institute Research Fellow) and will be reported elsewhere. This study revealed the presence of elongated complexes of molecular weight of the order of 1 million [4].

X-Ray Observations

The x-ray patterns of silk fibroin have been much studied since the original work of Brill [2]. Several unit cells are compatible with the data [16], but all interpretations agree that the polypeptide chains must be nearly fully extended and must lie parallel to the fiber axis. The identity period along the axis is 7 Å. and seems to correspond to the length of two amino

acid residues. The x-ray pattern of the stretched gland is identical with that of fibroin spun in the normal way. The dried unstretched gland was at first thought to give only a disoriented version of the fiber diagram [23].

Simizu [20] first and later Kratky, Schauenstein, and Sekora [10] found, however, that when carefully dried, the unstretched gland gave a recognizably different pattern from the disoriented fiber. Simizu called the two patterns α and β silk, and Kratky *et al.* silk *I* and *II*. Kratky's nomenclature will be followed to avoid an implication of similarity between the silk patterns and the familiar α patterns of hair, etc. In the present investigation x-ray patterns were made of most preparations by Mr. F. H. Meyer (T.R.I. staff member), and the existence of these patterns was confirmed and their occurrence more fully studied. The characteristic spacings of silk *I* and *II* as determined in this work are given in Table IV.

Discussion

The histological studies of the silk gland were undertaken to determine the location of the two proteins, fibroin and sericin, in the gland, and to see whether they could be separated. Some earlier work indicated a segregation of the two proteins, whereas other investigators did not agree with this. Possibly the various races of silkworms are not identical in this respect. Only one variety of *Bombyx mori* has been examined in this work, and in this the segregation of the two proteins in the mature worm was definite and easily demonstrated in stained material or by polarized light microscopy. Fibroin only was found (see Figure 1) in the long convoluted posterior section of the gland, *S*; in the mid-section or storage vessel, *M*, the fibroin formed a core and the sericin surrounded it adhering closely to the cellular envelope, and the same separation was found to persist in the tapering anterior section, *T*, leading to the spinneret. This disposition of the two proteins can be accounted for if we assume that the fibroin core is the product of the cells of the posterior section and the sericin annulus of the cells of the mid-section [1], as is suggested schematically in Figure 6. In some races of silkworms, Yamanouchi [24] noted minor amounts of sericin in the cells of the posterior section, particularly in young worms. This observation shows that the cells constituting the envelope of the gland do not have one kind of secretory activity exclusively. Nevertheless, during the last few days prior to spinning, when silk formation is at its height, it appears that the two proteins are synthesized predominantly in separate regions of the gland, and this separation is the factor primarily responsible for the fact that the two secretions are spacially separate in the storage

TABLE IV. CHARACTERISTIC SPACINGS OF SILK *I* AND SILK *II*

Silk *I* (Å.)	Silk *II* (Å.)
	9.6
7.6	
5.6	
4.5	4.8
4.0	4.3
3.67	3.67
3.2	
2.8	2.84
2.5	
2.3	2.27
2.06	2.09

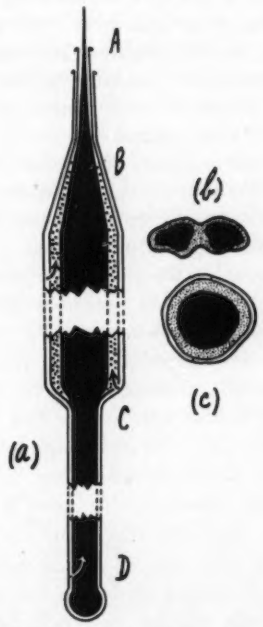


FIG. 6. (a) *Idealized longitudinal section of a silk gland.* AB *is the exit tubule leading to the spinneret,* BC *is the storage vessel, and* CD *is the secretory tubule. The fibroin is shown in black, the sericin is stippled. It is thought that the fibroin is secreted mainly by the portion* CD, *and the sericin by the walls of the vessel* BC. (b) *Cross section of spun silk thread showing the two fibroin fibers and the sericin surrounding them.* (c) *Cross section of the storage vessel of the gland showing fibroin core and sericin annulus.*

vessel (see Figure 6). A further factor impeding the mixing of the two liquids at their surface of contact is the strong coherence of the fibroin particles, which may be observed in the gland solutions and also in fibroin precipitated from extracts. This factor would tend to hold the fibroin core intact and would also tend to express peripherally any sericin which happened to become mixed with the fibroin solution. This same property, which lends a chewing-gum consistency to precipitates, has also been noted in regenerated feather keratin and wool keratin, which also readily yield coherent fibers.

The staining properties as well as the optical properties of the two protein solutions in the gland are different, enabling the two layers to be readily distinguished by means of the polarizing microscope. In the absence of mechanical distortion, the liquid (or fixed) fibroin core does not exhibit a strong or regularly oriented birefringence; this property only becomes marked as the liquid moves along the tapering exit tubule toward the spinneret. On stretching the fibroin core, the birefringence rises and the final thread is comparable in double refraction to the fiber extended in the ordinary way. Such threads also give a well-oriented x-ray pattern.

Somewhat surprisingly, the sericin annulus enveloping the fibroin of the storage section has a better developed optical anisotropy than the fibroin. The optical characteristics, as indicated in Figure 2, are of the film type—*i.e.*, the anisotropic elements appear to be randomly disposed in planes parallel to the gland surface. This disposition could be related to an expansion of the sericin layer and its compression against the cellular envelope due to the rapid growth of the central fibroin core in the last week of the worm's development. As the gland tapers anteriorly the two protein layers remain distinct, and the double refraction of the fibroin increases until it exceeds that of the sericin. Since the sericin annulus continues to envelop the fibroin right up to the spinneret, there does not seem to be any need for a special hypothesis to account for the fact that the sericin also surrounds the fibroin in the fiber after extrusion.

In addition to the two proteins, sericin and fibroin, raw silk contains small amounts of waxes and fats [illegible] yellow pigments [illegible] with the sericin annulus, and therefore presumably are secreted by the sericin-secreting cells. The yellow pigment is also mainly found in the sericin, but the fibroin is also pigmented. In freshly prepared extracts the pigment in the fibroin fraction sediments with the fibroin peaks, showing that it is associated with the fibroin molecules and is not independently dissolved in the solution. In aged solutions, however, the supernatant liquid remains colored, showing that the pigment-protein complex has dissociated.

The difference in solubility of the two proteins in sodium bicarbonate solution seemed to be great enough to be made the basis of a method of separating them. Direct observation of the process of dissolution showed that the fibroin core alone entered solution and left behind a hollow tube of sericin within the gland envelope. It is important for subsequent work to make sure whether any sericin is extracted also, and the above observations are not completely satisfying. The following considerations support the view that only fibroin precursors are present in the bicarbonate extract: (*1*) All three components are found by sedimentation analysis to behave similarly during the aging process leading to gelation, suggesting that they are all involved in a similar way in the process of fiber formation. (*2*) On shaking the solution and separating a portion of the protein, all three components are reduced in amount (the possibility of the adsorption of a nonfibrous protein onto the fibrous may rob this observation of certainty). (*3*) Sericin extracted from spun cocoons by warm bicarbonate extract has a sedimentation constant smaller than that of any of the components α, β, or γ. It corresponds more nearly to the slow component δ occasionally found in small amounts in the gland extract. (*4*) In strong solutions of urea the three peaks are reduced to one.

It will be provisionally assumed therefore that the three components (α, β, and γ) belong to the fibroin system, but it is hoped that ultimately a separation of the three will prove possible to establish this assumption more definitely. The important question then arises: Are these proteins three different proteins which combine to form fibroin in a manner recalling the formation of actomyosin [*22*], or are they aggregates of a single monomer molecule as is found

vessel (see Figure 6). A further factor impeding the mixing of the two liquids at their surface of contact is the strong coherence of the fibroin particles, which may be observed in the gland solutions and also in fibroin precipitated from extracts. This factor would tend to hold the fibroin core intact and would also tend to express peripherally any sericin which happened to become mixed with the fibroin solution. This same property, which lends a chewing-gum consistency to precipitates, has also been noted in regenerated feather keratin and wool keratin, which also readily yield coherent fibers.

The staining properties as well as the optical properties of the two protein solutions in the gland are different, enabling the two layers to be readily distinguished by means of the polarizing microscope. In the absence of mechanical distortion, the liquid (or fixed) fibroin core does not exhibit a strong or regularly oriented birefringence; this property only becomes marked as the liquid moves along the tapering exit tubule toward the spinneret. On stretching the fibroin core, the birefringence rises and the final thread is comparable in double refraction to the fiber extended in the ordinary way. Such threads also give a well-oriented x-ray pattern.

Somewhat surprisingly, the sericin annulus enveloping the fibroin of the storage section has a better developed optical anisotropy than the fibroin. The optical characteristics, as indicated in Figure 2, are of the film type—*i.e.*, the anisotropic elements appear to be randomly disposed in planes parallel to the gland surface. This disposition could be related to an expansion of the sericin layer and its compression against the cellular envelope due to the rapid growth of the central fibroin core in the last week of the worm's development. As the gland tapers anteriorly the two protein layers remain distinct, and the double refraction of the fibroin increases until it exceeds that of the sericin. Since the sericin annulus continues to envelop the fibroin right up to the spinneret, there does not seem to be any need for a special hypothesis to account for the fact that the sericin also surrounds the fibroin in the fiber after extrusion.

In addition to the two proteins, sericin and fibroin, cocoon silk contains small amounts of waxes and fats (about 1% by weight) and some yellow pigments. In this work these substances are shown to be present in the gland and must therefore also be secreted by the cells of the silk gland. The waxes, etc., are shown by x-ray examination [14] to be associated largely with the sericin annulus, and therefore presumably are secreted by the sericin-secreting cells. The yellow pigment is also mainly found in the sericin, but the fibroin is also pigmented. In freshly prepared extracts the pigment in the fibroin fraction sediments with the fibroin peaks, showing that it is associated with the fibroin molecules and is not independently dissolved in the solution. In aged solutions, however, the supernatant liquid remains colored, showing that the pigment-protein complex has dissociated.

The difference in solubility of the two proteins in sodium bicarbonate solution seemed to be great enough to be made the basis of a method of separating them. Direct observation of the process of dissolution showed that the fibroin core alone entered solution and left behind a hollow tube of sericin within the gland envelope. It is important for subsequent work to make sure whether any sericin is extracted also, and the above observations are not completely satisfying. The following considerations support the view that only fibroin precursors are present in the bicarbonate extract: (*1*) All three components are found by sedimentation analysis to behave similarly during the aging process leading to gelation, suggesting that they are all involved in a similar way in the process of fiber formation. (*2*) On shaking the solution and separating a portion of the protein, all three components are reduced in amount (the possibility of the adsorption of a nonfibrous protein onto the fibrous may rob this observation of certainty). (*3*) Sericin extracted from spun cocoons by warm bicarbonate extract has a sedimentation constant smaller than that of any of the components α, β, or γ. It corresponds more nearly to the slow component δ occasionally found in small amounts in the gland extract. (*4*) In strong solutions of urea the three peaks are reduced to one.

It will be provisionally assumed therefore that the three components (α, β, and γ) belong to the fibroin system, but it is hoped that ultimately a separation of the three will prove possible to establish this assumption more definitely. The important question then arises: Are these proteins three different proteins which combine to form fibroin in a manner recalling the formation of actomyosin [22], or are they aggregates of a single monomer molecule as is found in the fibrinogen-fibrin system, or are they configurational variants of a single molecule?

Aggregates of different s values, behaving not unlike those found here, were noted by Jullander [9]

in partly gelled systems of cellulose nitrate, and signs of aggregates in the keratin-forming system were also found by Mercer and Olofsson [15]. The best understood case is that of the blood protein fibrinogen, which resembles the silk precursors in the way in which it gels. If we are concerned with a phenomenon of aggregation, it is rather puzzling that there are only three peaks and not a whole series of peaks corresponding to a series of multiple aggregates culminating in insoluble fibril. The highly aggregated material, to which the greater part of the turbidity is due, sediments with great rapidity, and between this and the component α there is no other peak.

The different shapes of the sedimentation curves of the three components is another feature that is puzzling. The sharpness of β would imply that this molecule is more asymmetric than the others. This difference soon disappears as the solution ages, and there is a possibility, suggested by the variety of curve shapes actually observed in fresh solutions (presumably from worms of the same physiological age), that all the components originally have rather sharp peaks and that β alters less rapidly than α or γ. Certainly there is little to distinguish between them all after a few days have elapsed, since each peak has by then become very broad.

During aging the viscosity increases and the solution finally gels. There seems no reason to doubt that the molecular changes revealed by the ultracentrifuge are the cause of the increase in viscosity, but precisely what these changes are and how the modified molecules finally aggregate to yield asymmetrical fibrils is not yet clear.

The results of adding urea to the solution may be plausibly explained by assuming that the three components are formed from a single molecular species by a multiple association which is dissociated in strong solutions of urea. It is a problem to decide whether this association is a significant step in fiber formation—*i.e.*, whether the three components normally present in solution are the first members of a series of complexes leading to the fine fibrils detected electron microscopically in aged solutions. What little evidence bears on this question seems to show that these complexes are not steps in the building of the fibrous form. Fibrous strands can be formed very readily by shaking alkaline extracts having a sedimentation pattern quite different from the typical extract in neutral solution, and they can also be formed with more difficulty by shaking extracts in urea containing apparently only one component.

A dissociation of the complexes accompanied by a configurational change increasing the frictional resistance—*e.g.*, unfolding—is compatible with the observations. A slowing and broadening of the sedimentation curve also occurs on aging in alkaline solution, although the three peaks are poorly defined.

The molecular weights to be inferred from the data described in this paper are not very definite. The average diffusion constant could not be estimated directly because of the aging phenomenon, and the constants calculated from the width of the peaks during sedimentation are unreliable for the same reason. Furthermore, the sedimentation constant to be inserted in the Svedberg equation should be that at zero concentration, and there is evidence that s increases with dilution. The most direct determination was by light scattering [4], which gives a weight average of the several components. The calculated molecular weight (approximately 1,000,000) [4], although fairly reproducible, is probably too high, owing to the presence of the large aggregates detected in the ultracentrifuge. This difficulty is commonly met with in protein solutions in which aggregation occurs readily, and is likely to vitiate further scattering work on the silk system unless a method of stabilizing the original molecules is found.

Coleman and Howitt [3] found that the molecular weight of silk fiber dissolved in cupriethylenediamine was 30,000. Later, Holmes and Smith [8], also using cupriethylenediamine solutions of silk fiber, found s values between 2.3 and 2.8 in a 0.5% solution and diffusion constants in the range $1.6–3.1 \times 10^{-7}$ cm.^{2} sec.$^{-1}$. This work points to a considerably larger molecule than that proposed by Coleman and Howitt. Holmes and Smith still found only one broad peak, but the *average* s value of the three components (α, β, and γ) of the fresh gland extract is of the same order. It is probable that their solution approaches a genuine regeneration of the parent fibroin molecules. This opinion is strengthened by the observations of Happey, Hyde, and Manogue [7], who found that such solutions, after removal of the cupriethylenediamine, could be induced to generate fibrils similar to those formed by the gland extract. When the copper is dialyzed from these solutions they undergo a change leading to gelation, not unlike that occurring in the gland extract. It would be interesting to see what changes occur in the sedimentation pattern during this change. Similar properties are exhibited by a water-soluble synthetic, poly-*dL*-alanine, described recently by Elliott [5].

Evidence of intramolecular structural changes, which may be associated with the change from one type of H-bonding in an original molecule to another type in the aggregated form, is provided by the x-ray diffraction data.

Simizu [20], who first described the silk *I* pattern, and Kratky, Schauenstein, and Sekora [10] regard the silk *I* pattern as characteristic of the nonfibrous precursor (regarded as a single substance), and consider that the existence of the two patterns is proof of an intramolecular transformation occurring when the precursor changes into the fibrous form. The latter investigators were impressed by the occurrence of a spacing of 7 Å. in both the silk precursor and in actin, the muscle protein, which also undergoes a well-defined transformation from the soluble to the fibrous state. The implications, if any, of this coincidence remain obscure.

Since sedimentation analysis shows that more than one component occurs in the fibroin fraction of the gland, it is at least possible that the silk *I* pattern is not that of a single substance. This possibility does not alter the value of the observations as proof of changes occurring during fiber formation, but it shows that it is premature to try to deduce too much from the silk *I* pattern as it stands.

Summary

1. The solutions of the soluble precursors of sericin and fibroin are clearly segregated in the storage vessel of the silk gland of *Bombyx mori*, and may be distinguished by staining and by examination in polarized light, or separated mechanically after coagulation of the proteins. The solution of the fibroin precursors forms a core within the storage vessel, and the sericin envelops it. The same relative position occurs in the extruded fiber.

2. Dilute sodium bicarbonate solution extracts the fibroin core preferentially, and sedimentation analysis shows that the extract contains three major components, some aggregated material, and a variable amount of low-molecular-weight material. The three components, with approximate sedimentation constants of 1.8, 1.5, and 1, may represent precursors of fibroin, but there is insufficient evidence to show whether they are three different proteins, or multiple aggregates, or configurational variants of a single molecule. The addition of urea to the solution reduces the three peaks to one.

3. When a solution of the gland proteins is allowed to stand for some days it grows more turbid and viscous, and sets finally to a gel. This behavior is thought to be due to a slow transformation of the soluble proteins into the fibrous form. Shaking speeds this change and also leads to the separation of fibrous, birefringent threads.

4. During aging the sedimentation behavior is progressively modified. The sedimentation constants decrease and the spread of the individual peaks is increased, leading to very extensive overlapping just prior to gelation.

5. Light-scattering measurements indicate the presence of elongated particles of approximate molecular weight 1,000,000. This figure is probably strongly influenced by the presence of aggregated material. The sedimentation constants (< 2) of the major components point to somewhat smaller molecules, but molecular weights cannot be computed without diffusion constants.

6. The carefully dried fibroin solution from the gland yields an unoriented x-ray pattern (silk *I* pattern) different from that of the unoriented fibrous form (silk *II* pattern). Silk *I* has been thought to be the pattern of the nonfibrous precursor, but may not be the pattern of a single substance since three components are present.

7. The minor constituents of cocoon silk, waxes, and yellow pigments are also secreted by the gland and are mainly associated with the sericin fraction. The small amount of pigment in the fibroin extract is loosely associated with the protein.

Acknowledgment

The author wishes to acknowledge his debt to the Research and Development Laboratories, Philadelphia Quartermaster Depot, U. S. Army, for permission to use their ultracentrifuge; and to the Frick Chemical Laboratory, Princeton University, for the use of their Tiselius apparatus, electron microscope, and light-scattering apparatus. The author appreciates the very valuable assistance with the ultracentrifuge of Drs. Gail Miller and W. Stahl, of the Research and Development Laboratories. He wishes to thank his colleagues Dr. Richard O. Steele, Mr. Paul C. Colodny, and Mr. Frank H. Meyer for help in the laboratory and in discussion; Mrs. Luba Ross and Miss Dorothy O'Reilly for the drawings and photography; and Mr. Roy DeVeto, to whom the author is especially indebted, for tending the silkworms.

Literature Cited

1. Bergmann, W., TEXTILE RESEARCH **9**, 329 (1939).
2. Brill, R., *Ann.* **434**, 204 (1923); *Naturwissenschaften* **18**, 622 (1930).
3. Coleman, D., and Howitt, F. O., *Proc. Roy. Soc. (London)* **A190**, 145 (1947).
4. Colodny, P. C., private communication.
5. Elliott, A., *Nature* **170**, 1066 (1952).
6. Foà, C., *Kolloid-Z.* **10**, 12 (1912).
7. Happey, F., and Hyde, A. J., *Nature* **169**, 921 (1952); *Discussions Faraday Soc.* No. 13, 96 (1953).
8. Holmes, F. H., and Smith, D. I., *Nature* **169**, 193 (1952).
9. Jullander, I., "Studies on Nitrocellulose," Stockholm, Almquist and Wiksells Boktryckeri-A.-B., 1945.
10. Kratky, O., Schauenstein, E., and Sekora, A., *Nature* **165**, 319 (1950).
11. Lundgren, H. P., TEXTILE RESEARCH JOURNAL **15**, 335 (1945).
12. Mercer, E. H., *Nature* **163**, 18 (1949).
13. Mercer, E. H., *Australian J. Sci. Research* **B5**, 366 (1952); *Nature* **168**, 792 (1951).
14. Mercer, E. H., and Meyer, F. H., TEXTILE RESEARCH JOURNAL **23**, 243 (1953).
15. Mercer, E. H., and Olofsson, B., *J. Polymer Sci.* **6**, 671 (1951).
16. Meyer, K. H., "Natural and Synthetic High Polymers," New York, Interscience Publishing Co., 1942.
17. Meyer, K. H., and Jeanerat, J., *Helv. Chim. Acta* **22**, 22 (1939).
18. Ohara, K., quoted in "The Submicroscopic Morphology of Protoplasm and Its Derivatives," by A. Frey-Wyssling, New York, Elsevier Publishing Co., Inc., 1948, p. 197.
19. Rudall, K. M., in "Symposium on Fibrous Proteins," Leeds, England, Soc. Dyers Colourists, 1946, p. 15.
20. Simizu, M., *Bull. Imp. Sericult. Exp. Sta., Japan* **10**, 475 (1941).
21. Svedberg, T., and Pedersen, K., "The Ultracentrifuge," London, Oxford University Press, 1940.
22. Szent-Gyorgyi, A., "The Chemistry of Muscular Contractions," New York, Academic Press, 1947.
23. Trogus, C., and Hess, K., *Biochem. Z.* **260**, 376 (1933).
24. Yamanouchi, M., *J. Coll. Agr., Hokkaido Imp. Univ.* **10**, No. 4, p. 1 (1921).

(Manuscript received August 3, 1953.)

INDUSTRIAL SECTION

Static Electricity in Textiles*

J. W. Ballou

Textile Fibers Department, E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware

Introduction

There is no completely satisfactory understanding of the phenomenon of static electricity in textiles, but there is certainly enough known about its causes and effects so that a fairly consistent working theory is possible. Figure 1 shows the relations among the various fiber factors, the static charge, and finally the noticeable physical effects. This discussion will be concerned primarily with those physical effects that are objectionable from the standpoint of the wearer of textile fabrics. The cause of these symptoms is, of course, the electrical charge, Q. This charge usually results from pressure or rubbing contact of the textile material against other surfaces followed by separation. In addition to its magnitude, Q, this charge has two other measurable qualities of importance: the sign, whether plus or minus, and its rate of decay, or how fast it is dissipated. It might be argued that the rate of decay is more properly a quality not of the charge itself, but of the surface on which the charge rests, or the atmospheric conditions in its vicinity. This idea is partly true and will be expanded later, but for the time being decay will be associated with the charge itself for convenience. Those physical properties of the fiber or fabric that influence the qualities of the charge are surveyed in Figures 2 and 3. Figure 2 shows an idealized comparison of some of the different situations possible when static is generated. Each of the three cases involves what happens when two surfaces are pressed together and then separated, one surface being common to all three situations. In *A*, test surface #1 takes on eight units of plus charge, and

* Presented at a meeting of The Fiber Society in New Orleans, La., Apr. 22, 1953.

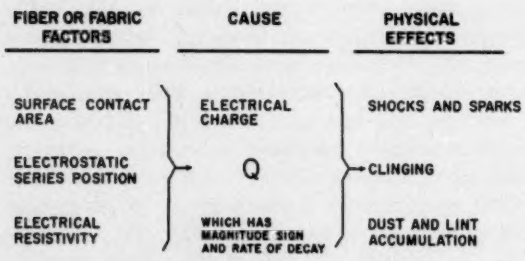


FIG. 1. *Static electricity relationships.*

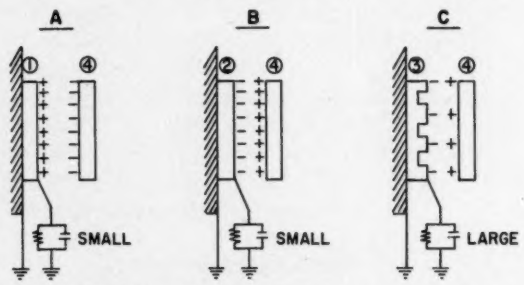


FIG. 2. *Typical situations involving static electricity.*

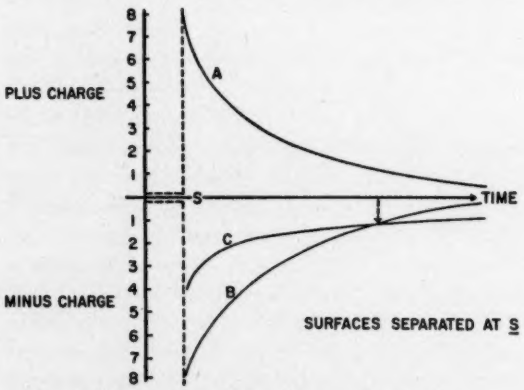


FIG. 3. *Change in charge with time.*

the common surface #4 eight units of minus charge. The test surface is assumed to have a small resistance and capacity to ground, actually through the material but indicated schematically as separate, so that charge leakage can take place relatively rapidly. In *B*, the only difference is that the test surface #2 takes on a minus charge. However, in *C*, a reduced area of contact results in only four units of minus charge, and a large resistance and capacity to ground results in a relatively slow leakage. The sign of the charge developed on the test surface is related to its position in the electrostatic series, which will be discussed later, the magnitude of the charge developed depends partly on the surface contact area, and the rate of leakage of the charge depends, in many cases, on the electrical properties of the material under test.

These charge qualities and the way in which they change with time for the three different situations depicted here are shown in Figure 3. The only difference between *A* and *B* is in the sign of the charge, whereas *C* is different from *B* in that the test surface has half the charge developed by virtue of the smaller contact area; this charge does not leak off as rapidly because of the larger resistance and capacity of the test surface with respect to ground. Note that in case *B*, in spite of the higher initial charge, the charge decays to a value equal to that on the test surface for case *C* after a certain time, and then becomes even smaller.

These considerations apply to textiles in general. Thus, it can be seen how fiber or fabric surface area of contact, electrostatic series position, and electrical conductivity are related to the electrical charge developed when textiles come in contact with or rub against surfaces such as human skin, leather, other textiles, metals, and other materials. The curves for cases *B* and *C* also show how one factor can compensate for another—*i.e.*, a fiber or fabric developing a large charge but having electrical characteristics resulting in a rapid charge decay may be the equiv-

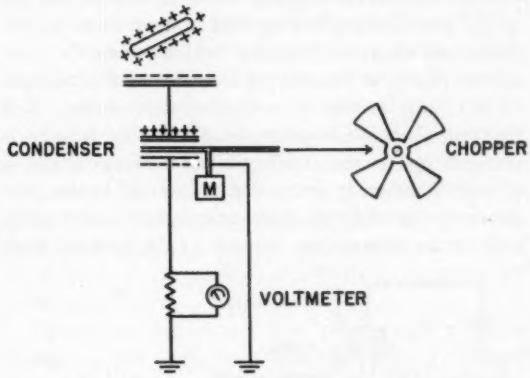


FIG. 4. *Schematic diagram of modulator.*

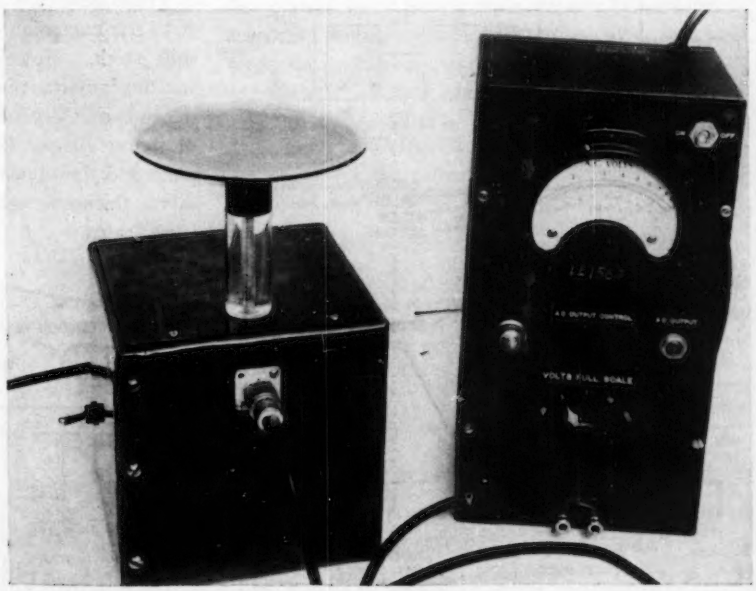


FIG. 5. *Photograph of modulator.*

alent, after a certain elapsed time, of one developing a small charge but having electrical characteristics resulting in a slow charge decay.

Instruments for Measurement

Two instruments, constructed in DuPont's Pioneering Research Laboratory, have proved very useful in studying static charges. Perhaps the most versatile of these is the sensitive detector copied after that developed by Havenhill, O'Brien, and Rankin [1]. This device is called a "modulator," because it modulates the electrical field set up by a static charge and therefore permits the use of alternating current amplifiers. Figure 4 is a schematic diagram of the modulator, showing that it consists of a condenser arranged so that the field between the condenser plates is interrupted by a grounded chopper or fan blade driven by a synchronous motor. If a charged object—for example, a piece of fabric—is brought up to the insulated top detector plate, a charge is induced, and a field is set up in the condenser. The chopper interrupts the field and thereby sets up an alternating current in the ground lead, which is measured by a voltmeter. This voltmeter reading indicates the magnitude of the charge on the fabric and is, of course, dependent on the proximity of the fabric to the plate. Figure 5 is a photograph of the device. The detector plate is visible, whereas the condenser and chopper are in the box. If, for example, a negatively charged object is brought near the plate and the plate is grounded momentarily, the plate will be charged positively. This charge will remain for a long time because the plate is well insulated. This positive bound charge, of course, results in a meter reading when the negatively charged object is removed.

If a positively charged object is then brought near the plate, the meter reading will increase; on the other hand, bringing a negatively charged object near the plate will result in a decrease in meter reading. Thus, the instrument permits measuring sign as well as magnitude.

To measure charge decay, the modulator is used with an amplifier and recorder, as shown in Figure 6. This arrangement records the decay with time or loss of a charge placed on the insulated upper plate of the modulator by virtue of its leaking through a fabric to a grounded weight. Examples of the rate of leakage to ground characteristic of various fabrics are shown in Figure 7. The same potential was put on the modulator plate in every case, so that the curves all start at the same voltage reading.

These fabrics were all about 7 mils in thickness, with the exception of the wool fabric which was 18 mils thick. However, differences in thickness are not too important in this test, since the rate of decay depends on the product of the resistance and capacity of the condenser formed by the charged modulator plate and the upper grounded plate. An increase of fabric thickness will increase the resistance but de-

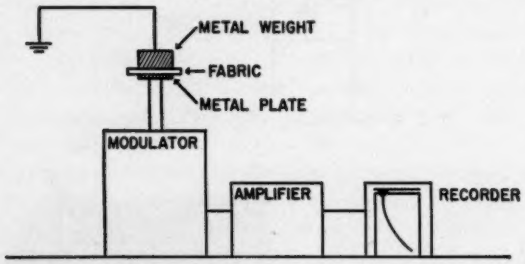


FIG. 6. *Using modulator to measure charge leakage.*

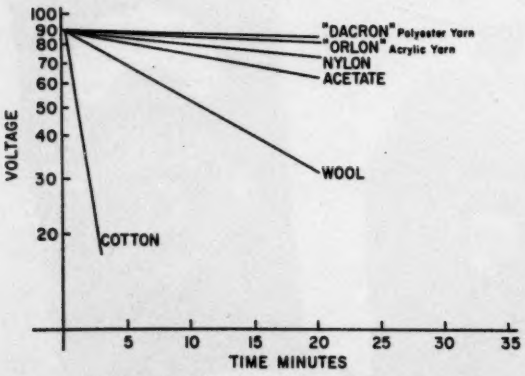


FIG. 7. *Charge leakage at 15% R.H. and 85° F through fabrics made from various yarns.*

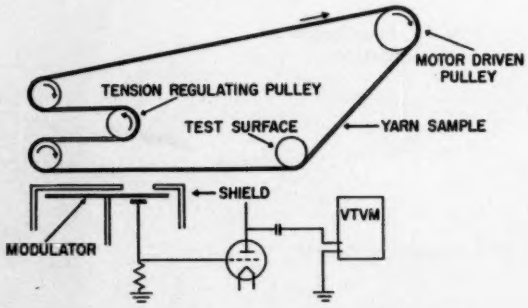


FIG. 8. *Static electricity tester for yarns.*

crease the capacity, so that the product remains a constant. This was checked experimentally by comparing the rate of leakage of three layers of fabric made from Dacron polyester fiber with that of one layer. No difference was found. The longer time for static charge to leak to ground through the fabrics made from hydrophobic fibers is graphically shown.

While the modulator just described is useful for measuring the magnitude, sign, and decay rate of static charges on fabrics, it is not particularly suitable for use with yarns. A device designed specifically to measure the static electrical properties of short lengths of experimental yarn is shown schematically in Figure 8. The sample is in the form of a closed loop of 400–500-den. yarn, 1.5 m. long. It is driven under a constant tension of about 0.25 g./den. over a standard surface. After passing over this surface, the yarn goes over an opening in a shielded can containing a modulated detector, which is similar in principle to the one just described and which "sees" a short section of the yarn through the opening. In practice, an aluminum test surface is used, because it gives results in accord with subjective static ratings and differentiates well between yarns. The yarn is moved in short spurts in between readings; the readings are taken with the yarn at rest. The device is calibrated by replacing the yarn with a section of insulated copper wire, and applying a known potential. Since temperature and humidity have a large effect, the device is enclosed in an automatically controlled humidity chamber.

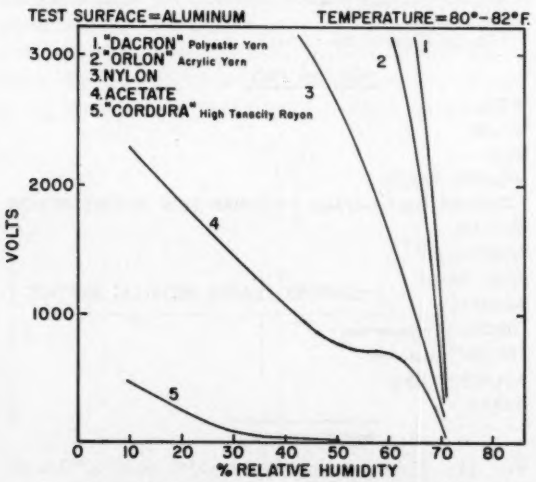


FIG. 9. *Initial charge build-up of various fibers.*

Figure 9 shows how various continuous-filament yarns compare in initial charge build-up at various relative humidities. The yarns, all between 400 and 500 den., were dry-cleaned, scoured, and then rinsed in changes of warm distilled water until the conductivity of the rinse water remained constant. The voltages developed represent the maximum readings before charge decay had a chance to set in.

At low humidities the voltage limit of the detector was exceeded in testing Dacron * polyester yarn, Orlon * acrylic yarn, and nylon. The relative voltages developed conform pretty much to what might be expected on the basis of subjective observations of these fibers in use, with the hydrophobic fibers developing the highest voltages.

To estimate charge decay rate with the apparatus used to obtain the voltage data shown in Figure 9, it is only necessary to note the time it takes for the voltage to drop to half its initial value. Figure 10 gives values of these times in seconds for the same well-cleaned yarns. The symbol ∞ is used merely to indicate that there was no perceptible charge decay in several minutes. These yarn data are consistent with those given earlier for fabrics made from the same yarns.

Figure 10 also shows that the leakage rate for charge on the four fibers with the highest voltages is negligible below 60% R.H., so that the steady decrease of voltage developed with increasing humidity for acetate yarn, for example, cannot be ascribed to increased leakage. It is noteworthy, also, that tests have shown that yarns slightly contaminated with, for example, oil may show an *increase* in voltage developed with increasing humidity, at least up to 60% R.H. These observations point to some effect of surface water other than increased electrical conductivity.

* DuPont trademarks.

YARN	RELATIVE HUMIDITY 30%	40%	50%	60%	70%
"DACRON" Polyester Yarn	∞	∞	∞	∞	∞
"ORLON" Acrylic Yarn	∞	∞	∞	∞	∞
NYLON	∞	∞	∞	∞	300-30
ACETATE	∞	∞	∞	∞	20
"CORDURA" High Tenacity Yarn	∞	300-30	10	0	0

FIG. 10. *Comparison of half-life of charge in seconds.*

The Electrostatic Series

In any electrostatic work the sign of the charge is of particular interest. It has been known for over two centuries that some charged materials are plus and some minus, after being rubbed or pressed against a common surface and separated. It has also been known that the sign depends on what the common surface is. An elementary way of looking at this is to say that some materials acquire a positive charge by loss of electrons because free electrons tend to leave these materials more readily than they do another surface, and a net loss results. Conversely, these same materials can acquire a negative charge if the other surface loses electrons more readily. It is important to realize that the process of electrification depends on getting good physical contact between the surfaces and, indeed, it has been proven experimentally that the charge developed is directly proportional to the area of contact. Friction or rubbing acts to promote this good contact so that the charge transfer can take place.

To investigate the sign of the charge developed in textile materials rubbed against various surfaces, including other textiles, yarn samples were boiled off, rinsed, and wound on plastic plates about 2 in. square. The samples were then rubbed together or against other surfaces so that the direction of motion was always parallel to the yarn axis. In every case, the samples were initially discharged with an ionizing source such as an Ionotron static eliminator.

The procedure for determining sign can be illustrated by an example. First, a bound charge of known sign—for this example, positive—is placed on the modulator detector plate so that a meter reading results. Then, if wound samples of nylon and cotton are rubbed together, separated, and brought in turn close to the charged plate, it is noted that the meter reading increases when the nylon is brought up and decreases when the cotton is brought up. This indicates that the nylon has a positive charge and the cotton a negative one. In this way, every possible contact combination of a group of yarns can be tested and a table prepared showing the results. Finally, this table can be consolidated into a consistent series called an "electrostatic" or "triboelectric" series, in which the yarns range from the one that is positive to all others in the group, down to the one that is negative to all the others, with the rest of the yarns arranged in between such that any member of the series is positive to those below it and negative to those above it. Such an electrostatic series at 15% R.H. is shown in Figure 11. It must be emphasized that many such series have been set up by various investigators, and that, at best, agreement is only approximate, because of differences in the manner of preparing the surfaces and other factors.

One noteworthy feature of this series is the chemical grouping of the fibers. At the positive end are fibers containing amide groups—*e.g.*, wool, nylon, and silk. At the negative end are the hydrocarbons and halogenated hydrocarbons—*e.g.*, polyethylene and Saran—with the hydroxy-rich polymers in between. It must be emphasized here that this series, as it was set up experimentally, ranks these yarns only as to sign; it is qualitative, and does not permit any comparisons of the magnitude of the charge.

As noted, this series holds at 15% R.H. A similar series of the same fibers at 60% R.H. is very little different from this, the only major change being a shift in the position of Fiberglas,* which moves up to a position between wool and nylon. Another interesting effect noted with glass is that a fire-polished glass rod rubbed with silk is charged positively, but if the surface of the rod is roughened with emery paper, then the rough surface takes on a negative charge when rubbed with silk; indeed, it is negative even to Orlon acrylic yarn. Undoubtedly different active chemical groups are uncovered by the abrasion in this case.

No discussion of the electrostatic series would be complete without some mention of the early work of

* Owens-Corning trademark.

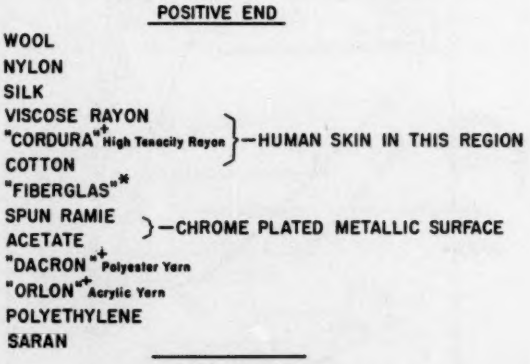


FIG. 11. *Electrostatic series at 15% R.H.* (**Owens-Corning trademark; + DuPont trademark*).

Coehn and Richards (discussed in [2], p. 32). These workers found that when liquids and solids are charged by contact with other solids, the material having the highest dielectric constant carries the greatest positive charge. This connection with dielectric constant is important because it ties in with certain observations which might otherwise seem anomalous and which seem more reasonable when it is realized that solids such as different textile materials and plastic films do not each have one unique dielectric constant. Instead, these may exhibit a range of dielectric constants depending on the amount of crystallinity and structural orientation present. If this were not the case, for example, polyethylene would never be expected to develop any charge when rubbed on polyethylene, and nylon would always be neutral to nylon. This is not always the case, and where charge is developed between like chemical structures, it can probably be related in every case, as Graham [2] pointed out, to differences in physical structure and therefore dielectric constant. For example, charge can be developed by rubbing together, along their axes, polymeric yarns of different draw ratio and, therefore, different structural orientations.

Perhaps even more interesting, it is possible to develop small charges in some cases by rubbing two samples of the same yarn together in such a way that their axes are crossed. Figure 12 diagrams this for nylon. In nylon it is observed that when the fibers are rubbed as shown—that is, the horizontal fiber rubbed along the axis of the vertical fiber—the vertical fibers takes on a small positive charge and the horizontal ones a small negative charge. This anisotropy is undoubtedly due to the different dielectric constants in the axial and transverse directions, but the fine details of the mechanism are not clear; the signs of the charges developed are affected by relative humidity, and some yarns show a reversal of sign compared to nylon. This anisotropy has been found in a great many yarns. It was not found in those cases where no very appreciable charge was ever developed anyway.

From an examination of the electrostatic series, the question naturally arises: How do blends of two fibers in this series behave as far as static is concerned? An example is the effect of blending Dacron polyester staple and nylon staple. In the electrostatic series shown in Figure 11, nylon is near the extreme positive end and Dacron is lower down in the series towards the negative end. If these fibers are rubbed individually—for example, against a chrome-plated metallic surface—the nylon develops a positive charge and the Dacron a negative one. In a staple blend of these two fibers this would still be true, as shown diagrammatically in Figure 13, which depicts the surface of an idealized blended yarn. Both signs of charge would exist simultaneously in close proximity, positive on the nylon and negative on the Dacron. In general, there would be a net positive or negative charge, and there would be very little tendency for the different charges to run together and neutralize each other since the fiber surfaces, in this particular case, are pretty effective nonconductors. However, a short distance away, the *fields* set up by these charges would tend to cancel each other—*i.e.*, the repulsive force experienced by a positively charged dust particle, due to one unit of positive charge on the nylon, would be cancelled

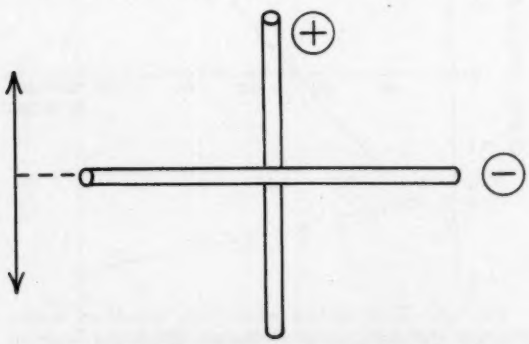


FIG. 12. *Electrostatic anisotropy in nylon.*

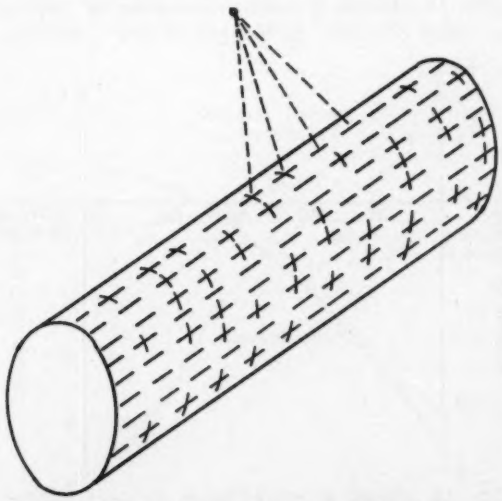


FIG. 13. *Static charges on surface of blended yarn.*

by the equal and opposite attractive force due to one unit of negative charge on the Dacron. The relative amounts of each sign of charge would, in a blend such as this, be controlled by the relative proportions of the two components and their relative chargeability. It was predicted that an absolutely neutral blend could be made in which just as many positive charges as negative charges are formed when the blend is rubbed against a third surface, providing the third surface has a position in the electrostatic series between the two components of the blend. Nylon, Dacron polyester staple, and a chrome-plated surface satisfy these requirements; therefore, a test was made to determine whether a zero net charge, neutral to the plated surface, could be found.

Nylon and Dacron staple were blended in a picker

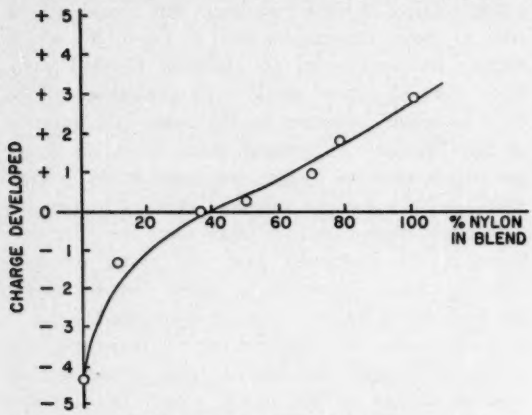


FIG. 14. *Blends of nylon-Dacron polyester staple—charge developed against chrome-plated surface.*

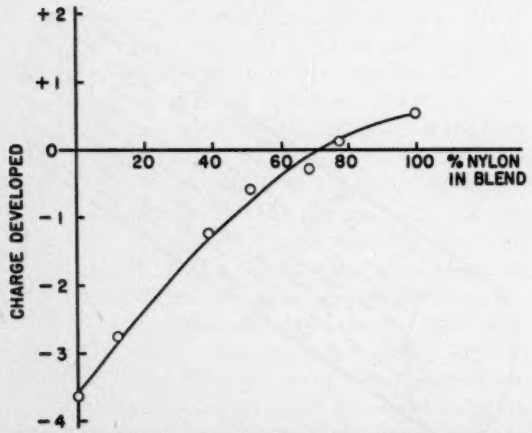


FIG. 15. *Blends of nylon-Dacron polyester staple—charge developed against cotton.*

in various proportions, carded, and spun into yarn. As the proportions approached equal amounts of each fiber, it was noticed that the static developed in processing, which was very noticeable with both 100% nylon and 100% Dacron, disappeared almost completely, an indication that the prediction was being fulfilled. Seven different compositions of spun yarns were thus obtained and tested for sign and magnitude of charge developed when rubbed over a chrome-plated metallic surface. The results are shown in Figure 14, where charge, in arbitrary units, developed under the conditions of the test is plotted against blend composition. As the percentage of nylon is increased, the charge goes from minus to plus, with a small composition range being essentially neutral to the chrome plate. Somewhere between 40% and 50% nylon content there is no net charge. Even though there are a large number of positive and negative charges, the blend is essentially static-free.

In the electrostatic series, cotton also has a position in between nylon and Dacron. This means that some blend composition of nylon and Dacron should be neutral to cotton also. Figure 15 shows the results of rubbing these same yarn blends against cotton, and it is seen that a somewhat higher percentage of nylon is required for neutrality—*viz.*, around 75%, compared with 40%–50% for the chrome-plated surface. This higher percentage is perhaps expected since cotton is nearer nylon in the series. The dif-

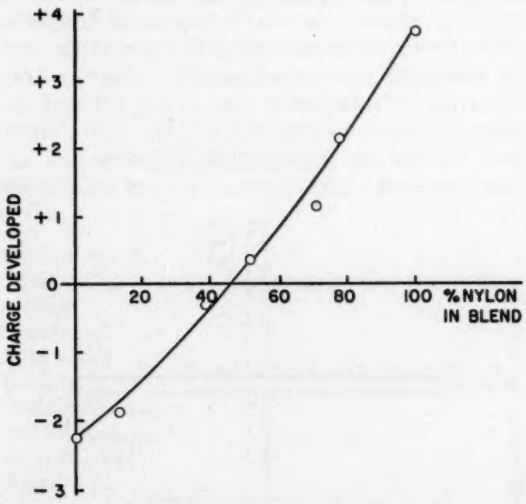


FIG. 16. *Knit fabrics made from blends of nylon-Dacron polyester staple—charge developed against chrome-plated surface.*

ferent compositions required for neutrality with the two different surfaces points up one of the drawbacks to blending for static reduction—the optimum composition varies from surface to surface.

These blends of nylon and Dacron polyester staple were made into knit fabrics that were tested similarly. Figure 16 shows that these knit fabrics behaved as the yarns did against a chrome-plated surface, with neutrality again requiring 40% to 50% nylon. Since wool is above nylon in the series, none of these compositions would be expected to be neutral to wool. Indeed, it was found that they were all negative to wool, as shown in Figure 17. To confirm the generality of this method of reducing static, a series of blends of nylon and Orlon acrylic staple were made and tested against various surfaces for sign and magnitude of charge developed. The results, in Figure 18, show that these blends behave similarly to the blends of nylon and Dacron, with the neutral composition only slightly different. Blends of nylon and Dacron and of nylon and Orlon containing about ⅔ nylon exhibit little static when rubbed against cotton.

In blends of wool and Dacron, the neutral composition, against the standard chrome-plated surface, contained 15% wool, as compared with about 50% nylon. This is what might be expected since wool is higher in the electrostatic series than nylon.

From this collection of data, it is possible to conclude that staple blending based on the electrostatic series is one way of reducing static in certain cases, but that the method is very limited because optimum compositions vary with the specific rubbing surface. However, since many common surfaces have positions in between the positions of fibers ordinarily used, no doubt some general improvement in static behavior would result. The most satisfactory blend is, of course, the one in which the fibers are mixed as intimately as possible, such as occurs in staple blends. Yarn blends, made by plying two different yarns, or weave blends, made by using one yarn as a filling and one as a warp, would be much less satisfactory. The distance away from the fabric at which electrostatic forces cancel out increases as the distance between the unlike charges increases.

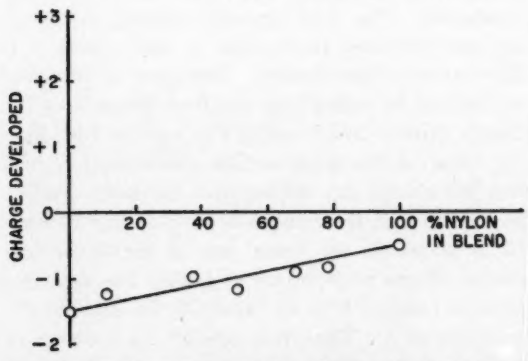


FIG. 17. *Knit fabrics made from blends of nylon-Dacron polyester staple—charge developed against wool.*

Fabric Electrical Conductivity

Charge decay by conduction through a fabric to a grounded surface is quite marked in the case of hydrophilic fibers because of their lower electrical resistance. In practice, this lower electrical resistance helps in the static reduction, even if no good ground in the electrical sense of a buried metal plate is available. A floor acts as a fairly good ground because of its capacity to absorb charge, while the human skin acts as a fairly good surface conductor to conduct charges to the floor through the soles of the shoes.

Electrical resistance through a fabric can be derived from the charge leakage curves shown previously by comparing the leakage through the fabric to ground with that produced by a standard one-million megohm resistor placed across the electrodes with the fabric in place. The resistance values so obtained naturally reflect the area of fabric used in the test, as well as the thickness of the fabric. In this work, a 1 in. square piece of fabric was used, and the results were reduced to megohms resistance per mil of fabric thickness. The resistances at various relative hu-

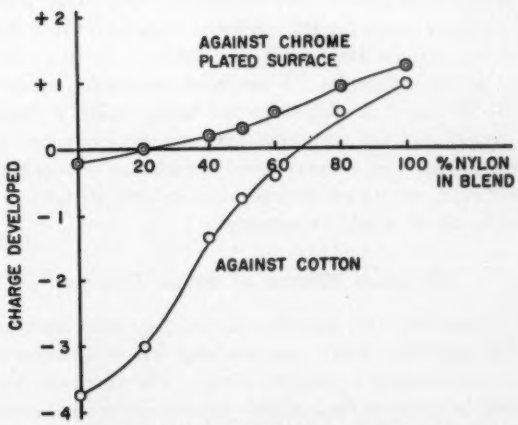


FIG. 18. *Blends of nylon-Orlon acrylic staple.*

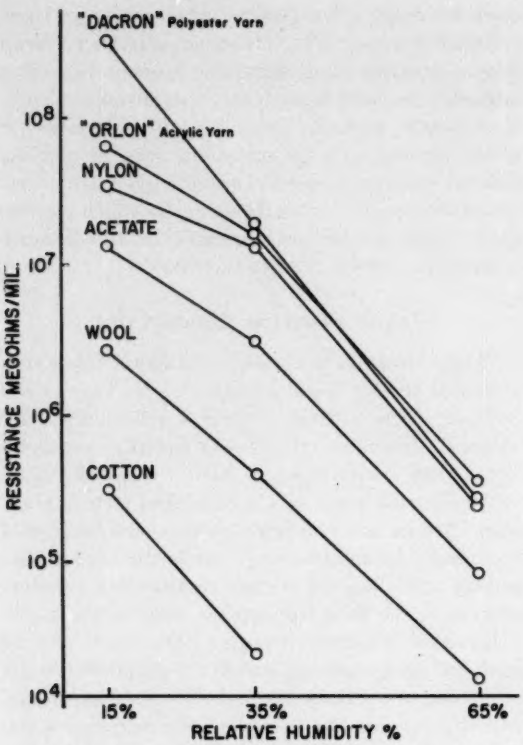


FIG. 19. *Resistances of plain-weave fabrics.*

midities for some typical plain-weave fabrics are given in Figure 19. Here it is shown that the electrical resistance through fabrics made from hydrophobic fibers is uniformly high compared to that through fabrics made from hydrophilic fibers. For treated fabrics with much lower resistances, it is found convenient to measure the electrical resistance along the fabric surface with a megohm bridge. In this case, a probe, consisting of insulated electrodes spaced .01 in. apart, is placed on the fabric under a given weight, and the resistance between the electrodes is measured. In general, good correlation was found between resistance through fabrics and surface resistance, as might be expected.

Physical Effects of Static Charge

There are two possible explanations why dust or lint particles, which are assumed to be insulators, are attracted to a charged fabric. The dust particles may be charged themselves—some positive and some negative—so that when they approach a charged

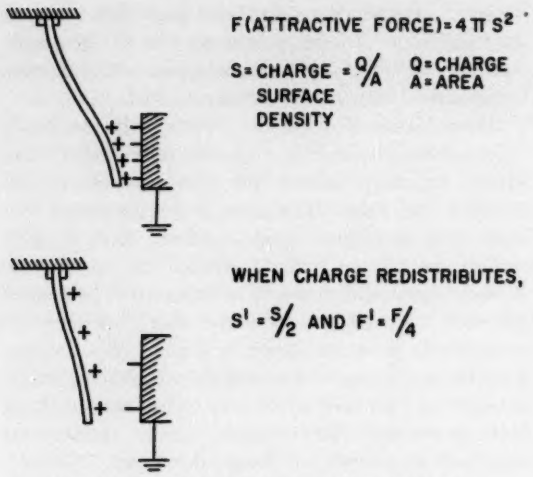


FIG. 20. *Electrostatic forces in clinging.*

fabric, the oppositely charged particles are attracted, obeying a fundamental law of electrostatics. If the particles are not charged, it is possible that electric dipoles are set up by the field from the charged fabric. These electric dipoles occur when the electrons bound to the atoms of the particle are slightly displaced by the force of the field, giving rise to an effective accumulation of opposite charge nearest to the fabric, with a resultant attractive force.

The clinging of fabrics to the skin involves some interesting concepts, which are explained by reference to Figure 20. Here is shown a fabric attracted to a grounded conductor, which could be the skin of the leg. Assuming that the fabric has momentarily rubbed against the leg and then become separated, so that it is charged on its lower portion, the situation is essentially equivalent to an electrical condenser. The field strength between the fabric and the conductor has a value of $4\pi S$, where S is the charge surface density. The force of attraction is obtained by multiplying the field strength by the charge density, which yields $F = 4\pi S^2$ as the clinging force. If the fabric surface conductivity is such that the charge can diffuse over the fabric surface in a short time, the result is a lower charge density. If, as shown in the lower part of the figure, the charge density is decreased to $\frac{1}{2}$, then the attractive force is reduced to $\frac{1}{4}$ by virtue of the squared dependence on S. Thus, it is possible for a charge to redistribute to a nontroublesome concentration, and clinging may disappear even though the total charge,

as indicated on a modulator, may remain constant. This effect has been noticed experimentally, and was a source of bewilderment until this possibility was realized. It is important to realize that, because of the nonlinear relation between force and charge density, clinging is not necessarily a good indicator of static development, although its practical significance cannot, of course, be discounted.

In addition to charge dissipation from a fabric being explained wholly in terms of its being redistributed or conducted to ground by the fabric surface, a fabric can also be discharged in other ways. For example, an ionic atmosphere produced by a radioactive source or even a flame can discharge a fabric by neutralizing the charges on its surface. A brush discharge is frequently observed when a highly charged ungrounded fabric is brought near the vicinity of a conductor. The individual fibers bristle stiffly and sparks fly. The reason this occurs is that a large concentration of charge always tends to collect on a sharp point, such as the end of a fiber; the resulting electrical field may be high enough so that the dielectric breakdown strength of the air will be exceeded and charges will be ejected from the fiber ends. If the fiber surface is a reasonably good conductor, the charges will be replenished by a flow along the fiber and charge will be lost quickly.

Thus, to summarize, there are several mechanisms by which charge density can be altered: the charges can be conducted to ground, they can diffuse over a surface and redistribute themselves, they can be neutralized by other charges, and, lastly, they can be lost by electrical discharge. Each one of these mechanisms has been observed with textiles in the laboratory. All undoubtedly play a role in actual wear, depending on circumstances.

Acknowledgment

All the experimental work covered in this paper was done by Mr. D. T. Meloon and Mr. J. A. Roetling. Dr. J. C. Smith contributed some of the ideas on the physical effects of static charge.

Literature Cited

1. Havenhill, R. S., O'Brien, H. C., and Rankin, J. J., Electrostatic Properties of Rubber and GR-S, *J. Applied Phys.* **15**, 731–40 (1944).
2. Graham, G. W., in the "Book of Papers for the Third Canadian Textile Seminar," The Textile Technical Federation of Canada, Montreal, Quebec, 1952, p. 32 ff.

(*Manuscript received October 8, 1953.*)

Improvement of Luster of Cotton

Part V: Fiber Shape in Relation to Luster*

Lyman Fourt, Ruth M. Howorth, Marjorie B. Rutherford, and Pauline Streicher

Harris Research Laboratories, Washington, D. C.

Abstract

The flattened, twisted-ribbon shape of the natural cotton fiber is unique among textile fibers, and leads to characteristic differences in the reflection of light from cotton, in comparison with that from more rounded fibers. With natural cotton, there are a large number of small planes set at every possible angle, so that light is not merely scattered, but also is in part reflected in a regular mirror-like way at every angle. However, small planes which are set at the more glancing angles reflect a larger proportion of the light which falls on them, in a manner described quantitatively by Fresnel's law. This explains the shift of the peak of reflection to angles higher than the mirror angle for the general surface, a shift which is greater for cotton than for most other fibers. If corrections based on Fresnel's law are applied, the peak of corrected reflectance is found to be at the mirror angle for cotton.

The relations between luster and the balance between regular reflection and scattering are also shown in the higher luster of sheer fabrics and the decreased luster caused by increased scattering from deeper layers. Another demonstration of the favorable effect of decreased scattering on luster is shown by the increased luster of dark colors, where absorption prevents scattering and leaves the field dominated by surface reflection.

In fabrics, there is scattering by the crossways system of yarns. If the Fresnel corrections are applied, the effect of the crossways yarns can be largely removed, and the effect of weaving crimp made clearer. Weaving crimp produces secondary or shifted peaks of reflection close to and on each side of the main peak, which correspond to the yarn rising up, going over the cross-yarn, and dipping down again.

Introduction

Cotton textiles must compete in appearance as well as in performance with man-made fibers, both in spun-staple form and in continuous-filament form. A silklike luster can be produced in sheer cotton fabrics by special treatment, and a great increase in luster can be produced in heavier cottons, but even so there are characteristic differences between the appearance of cottons and other textiles. Many of these differences have their origin in the special shape of the natural cotton fiber, which is retained to some degree even after mercerization.

This special feature of shape is the flattened, twisted-ribbon structure of the individual cotton fiber, which serves to distinguish it at once from all other fibers when examined under the microscope.

Consideration of the small elements of relatively flat surface on cotton fibers is useful in understanding the range of possibilities for improving the luster of cotton, in relation to other fibers. It also leads to an explanation of the shift of peak of maximum reflection away from the angle for mirror-like reflection, a puzzling feature of the reflection from fabrics. Displacement of the peak was pointed out by Quynn, Bernet, and Fischer [8], although in their observations, which were made with a different experimental arrangement, the peak was nearer to the normal, while in all the observations in the present work, the peak was farther from the normal than the mirror angle.

In fabrics the peak is even more obscured or shifted than in yarns, but use of the Fresnel correction factors indicates the presence of the peak and its location at the expected mirror angle to the general surface. In addition, secondary-peak tendencies arising from weaving crimp can be seen more plainly by use of the Fresnel corrections.

Sheer fabrics appear more lustrous because less light is scattered by multiple reflection and refraction

* A report of work done under contract with the U. S. Dept. of Agriculture and authorized by the Research and Marketing Act of 1946. This contract is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

Parts I–IV appeared in the July 1951, Jan. 1953, and Jan. 1954 issues of TEXTILE RESEARCH JOURNAL. Part VI appears in this issue, p. 163.

within the depth of the yarns. This effect is noticeable even with unmercerized natural cotton.

In addition, dyeing cotton to progressively darker shades, so that the light which penetrates the fibers is absorbed rather than reflected and scattered, shows the relative effect of surface reflection and external shape in comparison with the combined effects of internal structure and the scattering accompanying the penetration and return.

General and Detailed Views of Reflection

In measuring luster, it is convenient, for purposes of specifying the angle of view and the angle from which light comes, to regard the specimen surface as a uniform plane and to indicate angles with respect to the normal—that is, to a line at right angles to the plane of the general surface. Thus, the reflectance for viewing at 45° and illuminating at 45°, a set of angles which satisfies the condition for mirror-like reflection from the general surface, is designated as "45°, 45° reflectance," and the reflectance for viewing at 45° and illuminating along the normal is designated "45°, 0° reflectance." The ratio (45°, 45° reflectance)/(45°, 0° reflectance) for yarns arranged parallel to the path of light is called the "contrast ratio," and is used as a convenient physical measure of luster.

However, a more detailed view is required in considering the effects of fiber shape on luster, since here one must consider reflections from the tiny elements of the fiber surface or interior as well as the effect of curvature of the fiber surface and of irregularities which are too small to reflect but, rather, act as point sources and scatter light in all directions. In addition, the fibers are usually twisted into yarns, introducing another set of curvatures.

Experiments and Results

Geometry of Yarn Surfaces

If the specimen surface were composed of uniform, polished cylinders, the peak of reflection would be at the same angle as for reflection from a flat mirror, an angle equal and opposite to the angle of incidence, as shown by the geometrical analyses and experiments of Denham and Lonsdale [2], Foster [3, 4], and Pelton [7]. The observations of these workers have been confirmed by measurements on a winding of wire. For these smooth cylinders, it is easy to see that the arrangement of yarns or wires which will give maximum reflection is that in which the yarn or wire direction is parallel to the plane of the path of the light. For twisted yarns, however, the situation is not so easy to predict.

However, Foster [4] showed that for twisted, multifilament yarns, the yarn arrangement for maximum reflection is still that with yarns parallel to the path of the light, not that with fibers parallel, as might have been expected. This has been tested experimentally with cotton yarns of two degrees of twist and two yarn numbers. Representative results given in Table I show that there is no marked trend of amount of reflection with fiber angle in cotton yarns. If anything, the 45°, 0° reflectance may show a broad maximum which includes the fiber angle, but the mirror angle reflectance, 45°, 45°, is larger in the yarn direction, so that the largest ratio of the two reflectances is the usual contrast ratio, observed with yarns parallel to the path of the light.

Geometry of Cotton Fiber Surfaces

Going from yarns to still smaller surface elements, the characteristic appearance of cotton under the microscope suggests at once that the detailed surface of a cotton fiber must resemble a collection of tiny planes set at all possible angles. Hence, for a large number of cotton fibers viewed together, every combination of angle of view and illumination will be a mirror-angle combination for a certain number of

TABLE I. REFLECTION FROM COTTON YARNS—EFFECT OF ARRANGEMENT OF YARN PARALLEL TO LIGHT, OR SURFACE FIBERS PARALLEL *

Twist multiplier	Angle of surface fibers (degrees)	Angle of yarns (degrees)	Reflectances 45°, 0°	Reflectances 45°, 45°	Ratio of reflectances
3.0	23	0	73	106	1.45†
		20	74	104	1.40
		22	74	103	1.39
		25	73	103	1.41
		28	73	101	1.38
		30	72.5	99	1.36
4.0	26	0	72	101	1.40†
		20	74	99.5	1.34
		22	73	98	1.34
		25	73	98	1.34
		28	73	98	1.34
		30	73	96	1.31

* Cotton 30/1 yarns of 81% maturity, supplied by Mr. L. A. Fiori, of S.R.R.L.

† The usual "contrast ratio."

tiny planes. From this it is reasonable to expect that there will be a great deal of scattering by small but regularly reflecting elements in cotton, as well as scattering by curvature and by point sources. It is reasonable to expect that the lining up of fibers will impose a certain major trend on the orientation of the tiny surfaces, and that this distribution may be a typical normal probability distribution.

If so, one might expect that the curve of reflectances at a constant angle of view, such as 45°, for yarns parallel plotted against changing angle of illumination would look like a normal probability curve, with the peak at 45°. Such is not the case; the three curves of Figure 3 of Part I of this series [5] all show peaks beyond 45°. Although the peak is sharper and closer to 45° the more lustrous the yarn, it is evident that the slopes on the two sides of the peak are different and that the curve is only a rough approximation to the shape of the probability curve.

Fresnel's Law Effect on Reflectances

The direct representation of the measured reflectances fails to take account of the change of the fraction of light reflected as the angle of incidence changes. There is a certain amount of reflection from transparent surfaces, even though most of the light goes through, as one can realize from reflections seen in window panes. The quantitative relations are expressed in Fresnel's law [6], which applies to transparent, nonmetallic materials, such as glass or cotton.

The fractional reflectance can be calculated from the angle of incidence and the ratio of the refractive indexes of the materials on each side of the surface. Moon published tables [6] which give these reflectances for a series of refractive indexes and for angles measured in radians. While cotton has two refractive indexes, 1.580 and 1.533 [1], the effect of inclination of fibers due to twist is such as to make an average value of 1.55 useful. In applying Fresnel's law, it is necessary to distinguish between the angle of illumination or viewing, referred to the general surface, and the local mirror angle for the sets of tiny planes to which Fresnel's law is being applied. When one views the general surface at 45° and illuminates it at angle $a°$, the local mirror angle is $(45° + a°)/2$. In this expression, $a°$ is positive if on the opposite side of the normal to the general surface and negative if on the same side as the angle of view. Table II gives the fractional reflectances for a series of local mirror angles, calculated from Moon's publication, for refractive index 1.55. For convenience, under the usual conditions, in which the general surface is viewed at 45°, the series of angles of illumination with respect to the general surface, which correspond to the local mirror angles, is given in the first column, and the ratio of the fractional reflectance at each angle to that at 45° view and illumination is given in the last column.

The last column of Table II can be used to correct the observed reflectances for the Fresnel effect—that is, for the increased effectiveness of reflection at higher or glancing angles. Let R_a = observed reflectance from general surface, at angle of illumina-

TABLE II. REFLECTION FROM TINY PLANES, LOCATED SO AS TO GIVE MIRROR-LIKE REFLECTION AT EACH COMBINATION OF ANGLES WITH RESPECT TO THE GENERAL SURFACE *

Angle of illumination (degrees)	Local mirror angle (degrees)	Fraction of incident light reflected *F*	Correction ratio *C*
45†	0°	.04663	.8139
20†	12.5	.04667	.8141
15†	15	.04671	.8148
10†	17.5	.04678	.8161
5†	20	.04692	.8185
0	22.5	.04709	.8212
5	25	.04735	.8259
10	27.5	.04772	.8324
15	30	.04855	.8486
20	32.5	.04907	.8560
25	35	.04968	.8665
30	37.5	.05095	.8887
35	40	.05268	.9188
38	41.5	.05385	.9393
40	42.5	.05468	.9539
41	43	.05515	.9620
42	43.5	.05565	.9707
43	44	.05618	.9800
44	44.5	.05675	.9899
45	45	.05732	1.0000
46	45.5	.05795	1.0109
47	46	.05858	1.0218
48	46.5	.05950	1.0379
49	47	.05995	1.0457
50	47.5	.06054	1.0562
52	48.5	.06232	1.0807
55	50	.06500	1.1338
60	52.5	.07042	1.2284
65	55	.07736	1.3489
70	57.5	.08600	1.5002
75	60	.09716	1.6948

* All calculations are for view at 45° to the general surface and illumination at the indicated angles, for refractive index 1.55.

† Angles on the viewing side of the normal to the general surface.

tion $a°$, viewing 45°; F_a = fraction of incident light which is reflected by a plane set for mirror-like reflection between $a°$ and 45° (tabulated in Table II); F_{45} = fraction for a plane set parallel to the general surface, illuminated at 45°, viewed at 45°; $C = F_a/F_{45}$ = correction ratio (last column in Table II); $R_c = R_a/C$ = reflectance corrected for Fresnel effect.

In this method of correction, the observed 45°, 45° reflectance is left unchanged. A family of curves of corrected reflectance will therefore show the same reflectance at 45° as the original data.

Test of Fresnel's Law Effect

Such a family of curves for a cotton yarn at two conditions of processing is shown in Figure 1. This shows the curves of directly observed reflectance and curves corrected by the ratio C, which leaves the 45°, 45° reflectance at the same level, but adjusts all the other reflectances.

Both the high-luster mercerized yarn, which showed a peak in direct observed reflectance, although this peak was shifted to an angle above 45°, and the low-luster natural yarn, which showed no peak in direct observed reflectance but only a continuing upward trend, show definite peaks, centering closely on 45°, in the corrected curves. Thus, the shift of peak, or the failure to show a peak which is often seen with yarns of low luster, can be accounted for by the effect of increased efficiency of reflection from the tiny elementary areas at the higher angles.

Effect of Mercerizing

The corrected curve for the mercerized cotton is not only higher at the peak, but also is narrower in relation to its height. This suggests that mercerizing may have altered the distribution of tiny planes, so that relatively more of them are lying in the yarn direction and fewer are distributed at other angles. This may in part be what happens, owing to the tensions involved in mercerizing. However, the effect of mercerizing in producing more rounded fibers will also tend to concentrate the light at the mirror angle and reduce the scattering to other angles by reducing the randomness of distribution of reflecting surfaces.

Effects with Yarns Crossways to Light

The discussion so far has been concerned with yarns parallel to the path of light; in fabrics, however, there will be an effect of the other set of yarns —those crossways to the light. Figure 2 shows direct observations on yarns arranged crossways, and calculations made in the same manner as for Figure 1. Three points may be noted regarding these results:

(*1*) In the direct observations, the amount of light reflected increases steadily with increasing angle above 0°, as would be expected for the greater effectiveness of reflection with larger angles of incidence.

(*2*) The corrected curves show a generally falling trend. This is interpreted as a shadowing effect, which decreases the effective reflecting area.

(*3*) The higher level of the mercerized yarns at larger angles probably reflects the fact that mercerized yarn tends to be smaller in diameter and more compact than the corresponding yarn prior to mercerization.

For the parallel arrangement of yarns there is, of

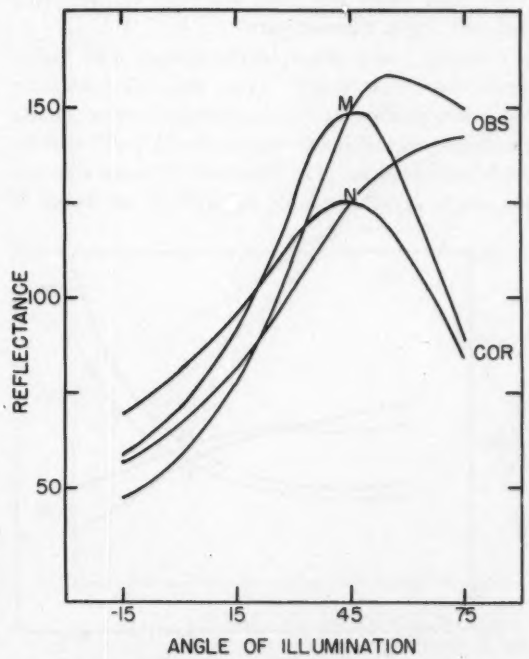


FIG. 1. *Fresnel effects with yarns parallel to the path of light. Acala 4–42 cotton, 40/2, natural* (N) *and mercerized at natural length* (M). *The curves marked* OBS *are direct observations of directional reflectance; those marked* COR *have been corrected for the increasing effectiveness of reflection at increasing angles, by means of Fresnel's law.*

course, very little shadowing effect, except at the fiber level, while for the yarns crossways arrangement of yarns this effect is large at the yarn level. Calculations based on spacing between yarns and yarn diameter could be made, but are complicated by the irregularity and uncertainty of yarn diameter. In fact, the data may be more useful as a method of determining average yarn diameter and its variability than for measurement of shadowing.

Comparison of Cotton and Other Fibers

The same type of correction has been applied to rayon staple yarns, with the results shown in Figure 3. These show that the mercerizing process makes the cotton more like bright rayon staple.

The effect of point-source scattering in the dull rayon is of interest in comparison with scattering both by planes and point sources in cotton, in that the peak for this type of scattering from point sources is broadened, especially towards the lower angles. This same effect has been observed in comparing dull and bright filament yarn.

Filament yarns show much sharper and higher peaks than staple yarns. Thus, the peak reflectance for a bright filament rayon measured under similar conditions was 883, and was at the 45°, 45° mirror-angle combination. The difference between this and the bright rayon staple of Figure 3 is attributed to twist and to the presence of numerous fiber ends in the staple.*

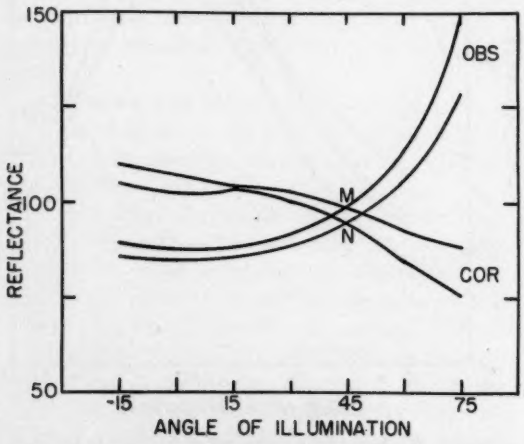


FIG. 2. *Fresnel effects with yarns crossways to the path of light. Same yarns as in Figure 1:* N, *natural; and* M, *mercerized at natural length. Curves marked* OBS *are direct observations of reflectance; curves marked* COR *have been corrected by means of Fresnel's law.*

Scattering and Reflection from Fabrics

The light coming from fabrics combines the effects of the yarns parallel and the yarns crossways systems, and introduces the additional complication of weaving crimp, so that the yarns parallel system does not run uniformly straight, but dips to go under and rises to go over the other systems of yarns, as well as showing a knuckle or a float across the top of the cross-yarns. The Fresnel corrections should be particularly useful in the study of fabrics, since, to a large extent, they can remove the effect of the cross-yarns in the region near and beyond the mirror angle.

* The orientation of individual fibers is also more regular in continuous-filament yarns than in staple yarns. Comparison of filament and similar staple at a series of twists would separate the regularity of arrangement and of fiber ends from that of twist alone. It is known that the effect of twist on the contrast ratio of filament yarns is very marked, especially in the low twist range. The bright rayon filament was 150 denier, 40 filament, S2.4 twist, 167 grex, or 35.4 cotton count, twist multiplier 0.4. The bright spun rayon was 30/1 cotton system, 19.7 t.p.i., twist multiplier 3.6, 197 grex. This suggests that the main factor here is twist.

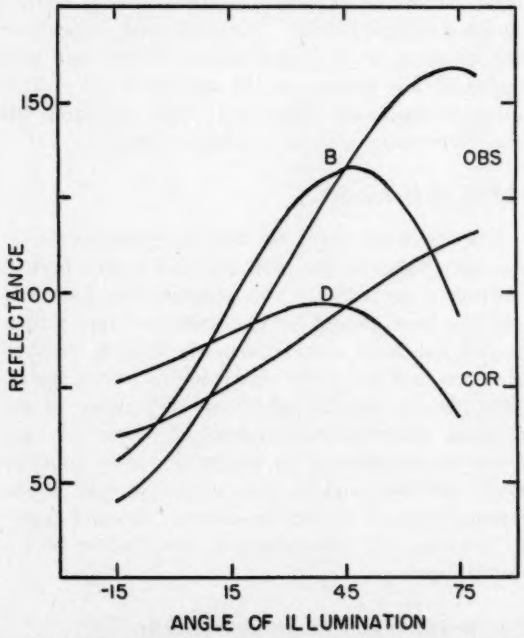


FIG. 3. *Fresnel effects with yarns parallel to the path of light. Staple rayon, bright* (B) *and dull* (D), *30/1 cotton count.* OBS, *observed;* COR, *corrected curves.*

Figure 4 shows a portion of the reflectance curve near 45° for an Oxford-weave fabric and the same data corrected for the Fresnel effect. When the Fresnel correction is applied, the data show a maximum at the mirror angle to the general surface and indications of secondary peaks such as would be expected from the effects of weaving crimp. Closely spaced observations are required to reveal these secondary-peak effects.

Scattering from Deep Layers

The lowering of contrast ratio in going from sheer conditions, with thin layers of fiber, to thick conditions, which reach a limit when absorption on the way in and out eliminates further change, has been explained in terms of increased scattering, by multiple reflection and refraction in the deeper layers. This should result in sharper peaks for thin layers, and flatter, broader peaks for thick ones. This is indeed the case, as may be seen in Figure 5, which compares one and seven layers of the same cotton yarn. The Fresnel corrections have not been applied to these data, so actual peaks are not seen, but the two sets of reflectances have been normalized by dividing each set by its 45°, 45° reflectance. This makes both curves pass through 1.00 at 45° angle of illumination. It is evident that the curve for one layer (cover factor 20) will show the sharper peak after the Fresnel corrections.

Surface and Interior: Effect of Color

An opposite effect to that of increased reflection from depth is to be expected if the absorption of light is increased by dyeing the yarn. A series of commercial mercerized sewing threads, one size and all from one maker, in white, increasingly heavy shades of grey, and black, are shown in Figure 6, as direct observations. In going to darker shades,

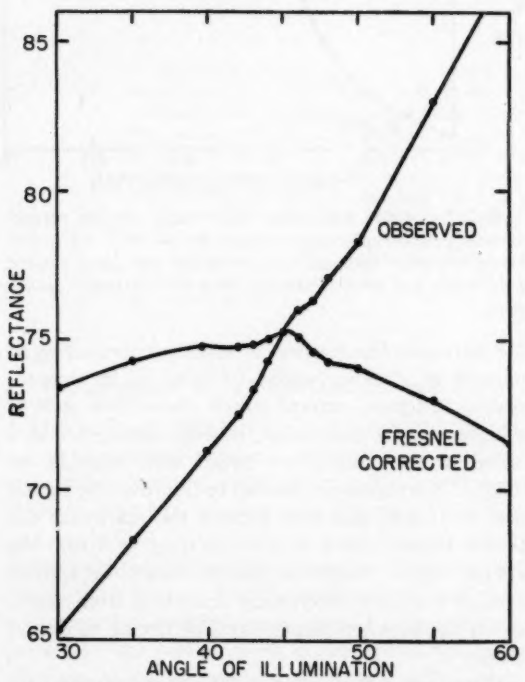


FIG. 4. *Combined effects of parallel and crossways yarns and weaving crimp in a fabric. The region near 45° is shown on a larger than usual scale. There is no maximum in the direct observations, but after correction for the Fresnel effect, there is a main peak and indications of secondary peaks attributed to weaving crimp. The fabric is Oxford weave, 88 ends, 42 picks/in., two warp ends woven together, 40/1 warp yarn, 15/1 filling, made available by Mr. R. J. Cheatham, of S.R.R.L.*

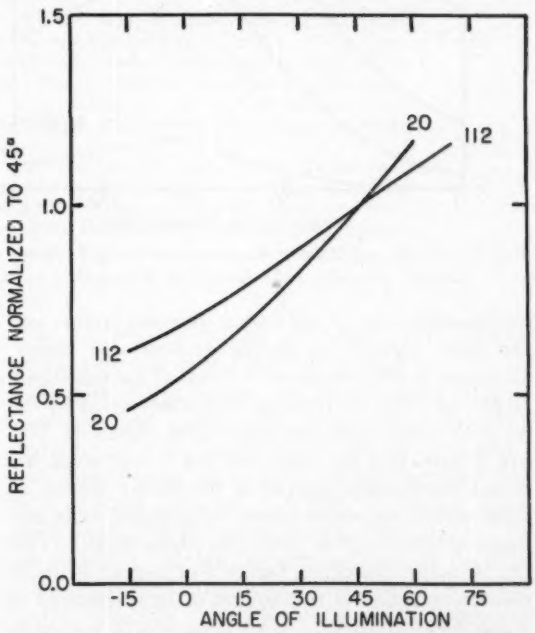


FIG. 5. *Effect of increased amount of cotton in increasing the scattering at angles away from the mirror angle, which is 45°. Reflectance curves for one layer, cover factor 20 (128 yarns/in.), and seven layers, cover factor 112 (104 yarns/in.), of the same yarn. Each reflectance has been normalized by dividing by the 45°, 45° relectance, which was 65 for cover factor 20, and 102 for cover factor 112. Deltapine cotton, natural, 42's, 3.5 twist multiplier.*

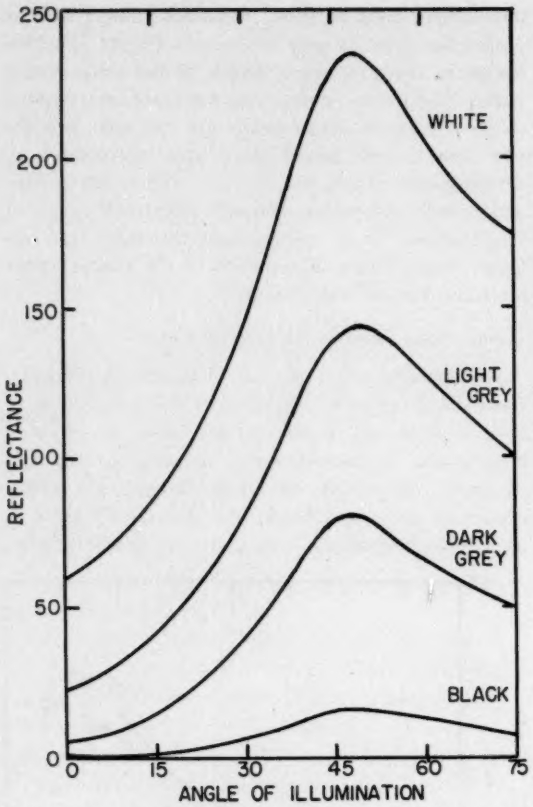


FIG. 6. *White and darker shades in mercerized sewing thread, showing reflectances as observed.*

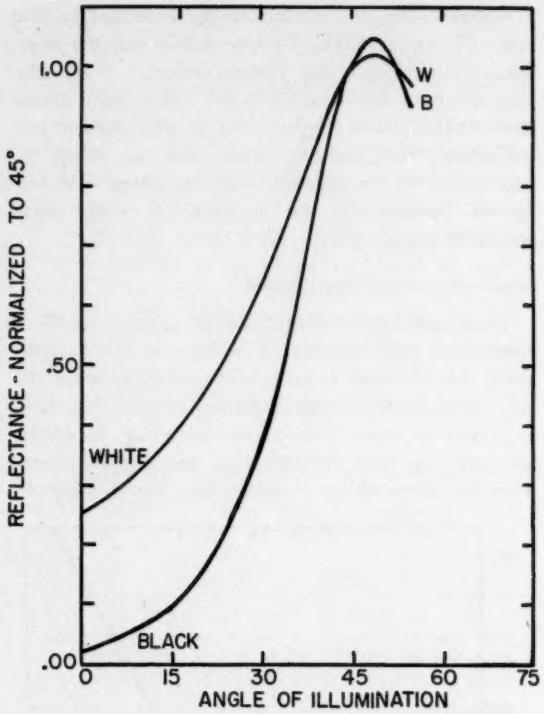


FIG. 7. *White and black mercerized sewing thread, showing each reflectance divided by the 45°, 45 reflectance for that material. The curves for grey shades, which are not shown, run between the extremes shown here.*

the general level of reflectance becomes lower, and the peak appears to become broader and flatter. However, if one normalizes in terms of the reflectance at 45° as unity, by dividing each observation by the 45°, 45° reflectance, the normalized curves of Figure 7 show that the peak near the mirror angle becomes increasingly sharper in the darker shades, as front surface reflection comes to dominate more and more completely over scattering from depth. This can be noticed in either Figure 6 or Figure 7, in the greater reduction of the amount of light scattered at angles away from 45°. This reduction of scattering is greater, in proportion to the scattering from white yarn, than the reduction of the peak, and so the contrast ratio increases.

Conclusions

The data shown here indicate that the shift of peak reflection or the absence of a peak in reflection from cotton yarns and fabrics can be explained by the increased effectiveness of small surfaces acting as mirrors at glancing angles. Owing to its twisted-ribbon structure, natural cotton shows this shift to a higher degree than other, rounder fibers, and in a different way than fibers dulled with titanium dioxide. Mercerizing is known to improve the roundness of cotton, and thus reduces the scattering due to tiny planes, aiding in concentrating light near the mirror angle. Sheerness also increases the appearance of luster, by decreasing scattering from depth, and a similar effect is produced by dyeing to darker shades.

When the reflection from fabrics is corrected for the change of effectiveness of reflection with angle, the effects of weaving structure are indicated as not one but three peaks of reflection.

Acknowledgment

The authors thank Mr. J. D. Dean and Mr. E. M. Buras, Jr., of the Southern Regional Research Laboratory for their aid in the supervision of this work.

Literature Cited

1. Am. Soc. Testing Materials, Appendix I in "A.S.T.M. Standards on Textile Materials," Philadelphia, 1942 and annually since then.
2. Denham, W. S., and Lonsdale, T., *J. Textile Inst.* **15**, T453–63 (1924).
3. Foster, G. A. R., *J. Textile Inst.* **17**, T77–81 (1926).
4. Foster, G. A. R., *J. Textile Inst.* **20**, T75–92 (1929).
5. Fourt, L., and Sookne, A. M., TEXTILE RESEARCH JOURNAL **21**, 469–79 (1951).
6. Moon, P., *J. Math. Phys.* **19**, 1–33 (1940).
7. Pelton, M. O., *Trans. Optical Soc. London* **31**, 184–200 (1929).
8. Quynn, R. G., Bernet, E. J., and Fischer, E. K., TEXTILE RESEARCH JOURNAL **20**, 492–509 (1950).

(Manuscript received August 26, 1953.)

Improvement of Luster of Cotton

Part VI: Yarn Structure in Relation to Luster*

Lyman Fourt, Ruth M. Howorth, Marjorie B. Rutherford, and Pauline Streicher

Harris Research Laboratories, Washington, D. C.

Abstract

The basic features of staple yarn structure which can vary in cotton yarns include those which depend on fiber factors such as fiber fineness, maturity, and staple length. Then there are mechanical processing factors, such as rate of carding, combing, and singeing, which affect fiber arrangement in or on the surface of the yarn. Finally, there are whole-yarn factors, such as twist, plying, and yarn fineness, which affect luster. These are discussed in three sections, which are presented together because of the use of experimental material which compares more than one type of factor at the same time.

The results show that the three main means of improving luster by yarn structure factors are: (*1*) lowering of twist; (*2*) use of optimum plying twist, as shown by Adderley and Oxley; (*3*) singeing to remove free surface fibers. Two additional structure factors, which, however, will not usually produce as great an effect on luster at the same cost, are: (*4*) using finer yarns; (*5*) combining.

Fiber Influences on Yarn Structure and Luster

The various individual physical properties of cotton vary together—to some extent randomly and to some extent systematically—so that it is much more difficult to isolate one variable at a time than in a man-made fiber. But while the most effective means of studying certain fiber properties in relation to yarn effects is by the use of artificial fibers, this also risks confusion by association of several properties: in particular, the present work indicates that the luster relations of cotton must be studied in cotton, since some of them depend on the unique flat, twisted-ribbon structure of the raw cotton fiber.

As part of this project, the interrelations of fiber properties and luster have been studied in yarns representing many types of cotton, both commercial and experimental, made available through the Bureau of Plant Industry, U.S.D.A. However, these yarns were spun at varying twists, depending on the staple length. Hence, as a preliminary to the general correlation of fiber properties and luster, it was desired to isolate, as much as possible, the effects of mechanical factors such as twist. Experimental material has been made available by the Southern Regional Research Laboratory. This material showed the effect of twist by itself; it was hoped that it might also show the effects of such factors as fineness or maturity and fiber length. Although the results show that there is reason to doubt that the effects

* A report of work done under contract with the U. S. Dept. of Agriculture and authorized by the Research and Marketing Act of 1946. This contract is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

Parts I–IV appeared in the July 1951, Jan. 1953, and Jan. 1954 issues of TEXTILE RESEARCH JOURNAL. Part V appears in this issue, p. 156.

TABLE I. FIBER FINENESS AND OTHER VARIETAL EFFECTS FOR CARDED YARNS SPUN FROM COTTONS CUT TO HAVE THE SAME LENGTH DISTRIBUTIONS *

Variety	Weight (μg./in.)	Yarn No.	Luster (contrast ratio) *TM* 3.5	Luster (contrast ratio) *TM* 4.25	Change of luster per unit of *TM* Nominal twist	Change of luster per unit of *TM* Measured twist
Tanguis	4.6	40/1	1.46	1.40	.080	.087
		40/2	1.60	1.54	.080	.068
Mesa Acala	3.3	40/1	1.45	1.39	.080	.058
		40/2	1.61	1.58	.040	.037
Seaberry Sea Island	2.9	40/1	1.52	1.47	.067	.066
		40/2	1.72	1.68	.053	.057
				Average:	.067	.062

* Yarns, fiber data, and nominal spinning data were obtained from Mr. L. A. Fiori, S.R.R.L. The cutter was set at $1\frac{9}{32}$ in. for Tanguis and at $1\frac{3}{16}$ in. for the others to produce equal distribution of fiber lengths.

of fineness and maturity have been separated from those of other fiber factors, it was possible to demonstrate the effect of fiber length by itself, and show that the effect of length is slight in cotton, although appreciable in longer-staple fibers.

Effect of Fiber Fineness and Other Variety Differences

Three cottons differing in fineness, or, its inverse, weight per unit length, as shown in Table I, were spun at the Southern Regional Research Laboratory at two levels of twist. These cottons were all cut to equalize fiber length distribution.

If the changes in luster are compared with the changes in fineness (Figure 1), it is clear that the relation, if there is any, is not uniform. The large change in luster comes in going to Sea Island, but this is the smallest change in fineness. The general level of luster for other cottons is determined by twist or plying, rather than by fiber fineness. Similarly, in the Bureau of Plant Industry series, American Egyptian cottons of a given length are higher in luster than long-staple upland cottons of the same length and fineness. This suggests that with the Sea Island, which shares many characteristics with the Egyptian cottons, the difference in luster is not due to fineness alone. It will be shown in discussing the effect of the combinations of fiber properties which characterize varieties and types that other fiber differences are much more important in setting Sea Island and Egyptian cottons in special classes.

Another line of evidence arguing against a connection between fineness and high luster in cotton is

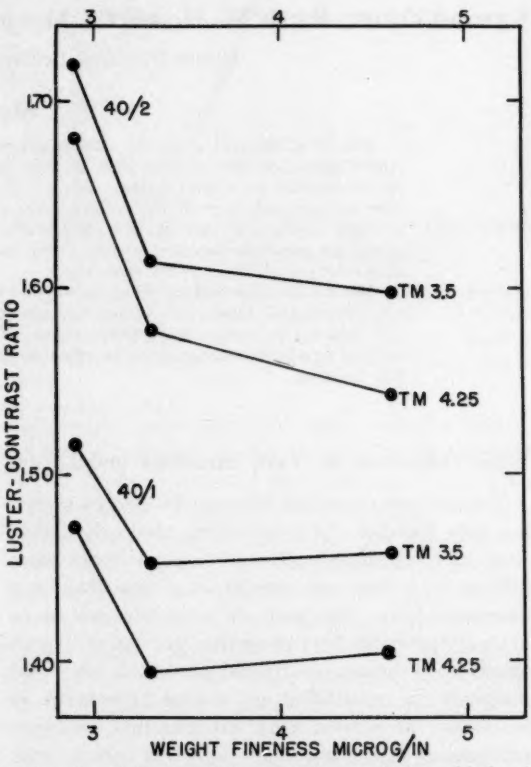


FIG. 1. *Luster and weight fineness of three kinds of cotton cut for uniformity of staple length. Singles and 2-ply yarns are shown at two levels of twist multiplier* (TM).

the fact that in man-made fibers, higher luster is obtained with the coarser deniers, since there is more regular reflection and less scattering. Similarly, the

TABLE II. MATURITY DATA FOR COTTON OF UNKNOWN VARIETY *

Yarn No.	Maturity = 55% Fineness = 4.0 μg./in. (Micronaire = 3.1) Luster (contrast ratio) TM 3.0	TM 4.0	Change of luster per unit of TM Nominal twist	Measured twist	Maturity = 81% Fineness = 5.2 μg./in. (Micronaire = 5.0) Luster (contrast ratio) TM 3.0	TM 4.0	Change of luster per unit of TM Nominal twist	Measured twist	Change of luster with increase of maturity for: TM 3.0	TM 4.0
14/1	1.40	1.34	.06	.071	1.41	1.35	.06	.065	.01	.01
22/1	1.44	1.39	.05	.058	1.44	1.38	.06	.067	.00	−.01
36/1	1.43	1.39	.04	.055	1.48	1.43	.05	.059	.05	.04
14/2	1.57	1.54	.03	.030	1.57	1.52	.05	.075	.00	−.02
22/2	1.58	1.54	.04	.049	1.60	1.55	.05	.059	.02	.01
36/2	1.60	1.55	.05	.046	1.61	1.55	.06	.064	.01	.00
		Average:	.045	.052		Average:	.055	.065		

* Fiber and spinning data were furnished by Mr. Louis A. Fiori, S.R.R.L.

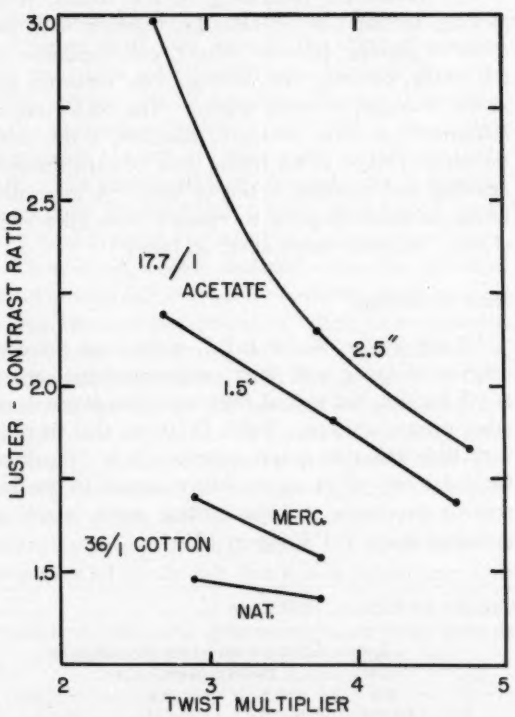


FIG. 2. *Effect of staple length, at three levels of twist, in acetate yarns. Natural and mercerized singles cotton yarns are shown for comparison.*

"luster" wools are long and coarse, although here the higher crimp of short fine wools complicates relations.

The probable absence of a basic relation between fineness and luster in cotton does not, however, mean that there is not a practical relation, since in cotton the long-staple varieties which can be spun into fine yarns of lower twist are also the finer fibers, and, in general, finer fibers are required if one is spinning fine counts or is near the spinning limit. As has been shown, the use of fine yarns and fabric sheerness both enhance luster.

Effect of Maturity

The possible effect of maturity might be expected to be related to that of fineness, since immature fibers are finer in terms of weight per unit length than mature fibers of the same variety. However, maturity is concerned with the wall thickness, while fineness is concerned in one sense with the reciprocal of weight per unit length and in another with effective diameter.

Two sets of cotton yarns made from cottons differing in maturity, for which fineness data were also determined at S.R.R.L., are reported in Table II. This series also included variation in yarn fineness and in twist, so that comparisons should be made between corresponding pairs at constant yarn number and twist factor. Of the twelve pairs, seven show an increase of luster with increasing maturity, three show no change, and two show a decrease. However, only two of the differences are larger than 0.02 in contrast ratio, and none are larger than 0.05, so that the influence of maturity or fineness as affected by maturity is small in this range. In the descriptive terms [8] used by the Cotton Branch, Production and Marketing Administration, U.S.D.A., this range is from "average" to "very immature."

Effect of Length

A third series of yarns spun at S.R.R.L. show the effect of fiber lengths as a single variable. These yarns were all from one lot of S × P cotton of 1.49 in. original length; after cutting, the upper-half mean lengths were 1.38 in. and 1.0 in., respectively, rather large differences in length for cotton. The results in Table III indicate that the effect of length by itself is small in cotton, ranging from 0.01 to 0.05 unit of contrast ratio for 0.5 in. difference in length.

The effect of length was also studied in a series of acetate staple yarns made available by Dr. Walter J. Hamburger of Fabric Research Laboratories. These yarns were described by Platt [7] who published staple arrays for the 1.5- and 2.5-in. staple removed from the yarns. The luster measurements on these (shown in Figure 2) raise two points:

(1) Comparison of 1.5- and 2.5-in. staple shows a marked increase of luster for the longer staple. There are, however, two differences from cotton: the range of length is greater and the general level of luster is higher.

(2) The effect of change of twist is very much more rapid in the acetate yarns than in cotton, either natural or mercerized. This is an example of the necessity of studying structure effects in cotton itself, since other factors are involved in using artificial fibers as models. In this case, it is probable that the difference arises from the greater amount of reflection at all angles by the small flat surface of the twisted-ribbon structure of cotton.

TABLE III. EFFECT OF LENGTH ON LUSTER (CONTRAST RATIO) FOR ONE KIND OF COTTON (S×P) CUT TO SHORTER LENGTHS *

	Upper-half mean length (in.)	Contrast ratio for the following yarn numbers: 20/1	20/2	40/1	40/2
Uncut control	1.5				
Spinning *A*		1.51		1.57	
Spinning *B*		1.52	1.80	1.56	1.83
Cut	1.38	1.50	1.77	1.55	1.81
Cut	1.0	1.50	1.75	1.56	1.79

* Spinning and fiber data were obtained from S.R.R.L. The twist multiplier for both singles and ply was 3.5.

Mechanical Processing Influences on Yarn Structure and Luster

The mechanical processing of the cotton, from picking, by hand or by machine, together with the mode of ginning (saw or roller), and variations in the baling, opening, and carding, may influence the luster of cotton to some degree. The major direct influences on yarn structure, however, come after the carding stage, as the cotton goes forward through drawing and combing if this is used. A quite different process—singeing to remove loose fiber ends—has a relatively large effect on luster.

Rate of Carding

All the cottons of the B.P.I. series used for correlation of luster with fiber properties were carded at 9.5 lbs./hr., but special tests were also available at other rates of carding. Table IV shows that there is very little effect on contrast ratio. It is difficult to recognize any effect on the luster caused by the increased neppiness at high carding rates, which is indicated in the B.P.I. report [3].

TABLE IV. EFFECT OF RATE OF CARDING ON LUSTER, 1950 CROP

Variety and location	Type of yarn	Luster (contrast ratio) for the following carding rates: 3.6 lbs./hr.	6.5 lbs./hr.	9.5 lbs./hr.	12.5 lbs./hr.
Hopi Acala 50, Shafter, Calif.	carded single	1.48	1.48	1.46	1.48
	combed single	1.46	1.50	1.51	1.52
	combed 2-ply	1.80	1.82	1.80	1.80
Acala 4–42, Shafter, Calif.	carded single	1.43	1.43	1.41	1.40
	combed single	1.47	1.44	1.43	1.45
	combed 2-ply	1.65	1.66	1.68	1.66
Delfos 9169, Stoneville, Miss.	carded single	1.40	1.40	1.40	1.39
	combed single	1.43	1.44	1.44	1.41
	combed 2-ply	1.64	1.60	1.65	1.63

Effect of Combing

One of the effects of combing is to remove shorter fibers. These results on cut cotton in Table III suggest that this might increase luster, though only by a small amount. In addition, combing should produce yarns in which the fibers are more nearly parallel, which would also increase luster. The corresponding carded and combed yarns of Table IV show eleven cases of increase of luster with combing, and only one decrease, averaging 0.03 unit of contrast ratio increase.

A series of similar combed and carded yarns, all of the same nominal yarn number and the same range of nominal twist, was furnished by S.R.R.L. The results on these (shown in Figure 3) also indicate a higher general level for the combed yarns.

Another set of data showing the effect of combing in comparison with carding was available from the B.P.I. series. In 88 specimens of cotton available both as carded and combed yarns (36's), the combed was higher in contrast ratio, on the average, by 0.022 unit. The distribution of contrast ratio differences is 69 pairs in which the combed was higher, eight with no difference, and eleven with the combed lower.

These three sets of evidence show that the chief effect of combing is not to be found in luster as such, unless the small lots examined, which were produced in spinning laboratories, are not representative of commercial production. This finding does not indicate that combing is not valuable for improving the strength and appearance of yarns, in removing neps, increasing evenness, cleaning the cotton, and permitting the spinning of fine counts, but it does indicate that at the middle level of counts (36's) the effect on luster as such is small. This conclusion is strengthened by the fact that it is in accordance with the very small effect of changes of fiber length produced by cutting.

Effect of Loose Fiber Ends and Their Removal by Singeing

Differences in staple length might be expected to affect luster through variation in the number and length of loose fiber ends per unit length of yarn. While the direct effect of length is small, a considerable change in luster is secured by removal of loose ends by singeing. This is shown by the data in Table V for a group of commercially spun yarns, in which the contrast ratio of the mercerized yarns was increased between 0.4 to 0.6 unit by gassing, a very substantial and noticeable increase.

It is worth noting that the effect of gassing is shown in the same way as that of mercerizing—by decreasing the scattered light, as shown by the 45°,0° reflectances, and increasing the light reflected at the mirror angle, 45°,45°. That the removal of fuzziness reduces the scattering might be expected, but the fact that it increases the mirror reflection indicates that more light can be concentrated by the smooth surface of the main body of the yarn.

TABLE V. EFFECT OF REMOVAL OF LOOSE FIBER ENDS BY SINGEING (COMMERCIALLY SPUN YARNS, ALL WITH LOW OR MERCERIZING TWIST)

Yarn No.	Cotton	Luster (contrast ratio) Natural	Mercerized	Mercerized, gassed
20/2	Combed Peeler, Carolina	1.63	2.40	—
40/2	C.P. blend Delta and Western	1.64	2.52	2.93
50/2	C.P. Acala	1.63	2.34	2.98

Whole-Yarn Structure Factors

Effect of Twist

The general effect that increased twist decreases luster is well known, and has been put to use in the dulling of hosiery by high twist. The other direction of the effect—to increase luster—is used in cotton practice, in the lower twist usual for mercerization in yarn form. Increase of luster is not the only factor in the choice of low twist for mercerizing, since penetration by the mercerizing liquor and suppleness

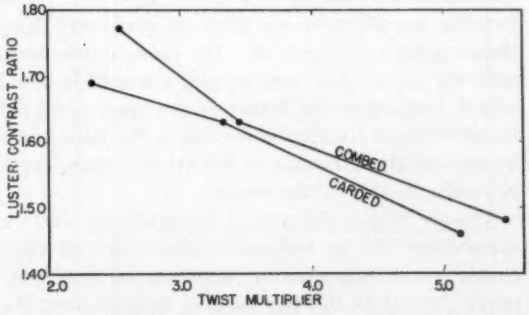


FIG. 3. *Comparison of luster in combed and carded singles yarns at three levels of twist.*

for knitting are also involved. However, even though the trend of the relation of twist to luster is well known, no quantitative information on this relation has been found.

Twist is most conveniently compared for yarns of differing fineness in terms of twist multiplier, M, defined as:

$$M = T/(N_c)^{0.5},$$

where T is the turns per inch and N_c is the yarn number in cotton count.

Method for Twist

Twist has been measured by a modification of methods 4052 and 4054 of Federal Specification CCC-T-191B [4]. The modification is designed to give results for the component singles of plied yarns which are more strictly comparable to the results on the ply as a whole, and to results on yarns which were originally singles, than might some others [2].

The yarn is inserted in the twist tester under the tension (156 g. divided by the equivalent singles yarn number) specified, and a weight is found which, being in the center of the specimen, will produce a conveniently observed deflection—0.05 in. for 10 in., used for singles, or 0.1 in. for 20 in., used for ply. This weight is made of wire in the form of a loop, so that the length can be adjusted to just touch or clear the rod of the twist measuring device while hanging on the yarn. The criterion of just touching or clearing is that less than one full turn in 10 in. shall make or break contact. Subsequent specimens are mounted with this central weight and deflection. The twist in yarns which are originally singles is determined by the untwist-reverse twist method, to give the same deflection on twisting in the opposite direction. The weight is removed until the reverse twisting has taken up the slack, to avoid stretching the yarn while at low twist. Ply yarns are mounted with the same initial tension, and a weight is found which, hanging at the center of the span, gives 0.1 in. deflection. Except for the sag of the yarn under its own weight, this ratio of deflection to gage length is similar to that of the singles.

The ply twist is determined by untwisting until the components can be separated; after this, the twist contraction is measured by adjusting the length between jaws until the two parallel strands show the same central deflection as the original ply yarn. The separate strands are then removed from the rotatable jaw and fastened to prevent loss of twist. The nonrotating jaw is then set at 10 in.; and the individual components of the ply are each tested as if they were original singles.

Range of Twist

Choice of twist multiplier is ordinarily determined on the basis of staple length, together with the intended use of the yarn, without direct regard to luster. A representative selection of twist multipliers [6] for 1-in. staple is: warp, 4.75; filling, 3.50; knitting, 3.0. Twist multipliers near 3.0 are also frequently referred to as "mercerizing twist." The test spinnings of the Production and Marketing Administration of the U.S.D.A. are designed to provide maximum yarn strength, and are based on upper-half mean length, varying by steps of 0.05 for, in general, each 0.03 in., from TM 4.10 at 1-in. staple. An exact table is given in [8]. A possible explanation of the difference is implied in the statement of Fiori and Brown [5] that in common mill practice, warp twist multipliers selected "are usually slightly higher than would be required for maximum yarn strength, in order to allow for processing variables."

The P.M.A. system of spinning is also used for the yarns of the annual varietal and environmental studies of the Bureau of Plant Industry, U.S.D.A., which are the yarns which have been examined in this program with the objective of correlating variety characteristics and luster. The range of twist multipliers in the 1949 and 1950 series of the B.P.I. is from 3.50 to 4.20, so it is within this range especially that the effect upon luster of twist alone is needed, for comparison with the effect of fiber properties and variety characteristics.

Experimental Results

Figure 3 illustrates the general relations between twist and luster, which, however, may be somewhat affected by fluctuations arising from small samples, these data being based on windings, each of which was made from one end of yarn. The data of Tables I and II are more valuable in this regard, since each value is averaged for yarn from twelve spindles. The tables show the change in contrast ratio per unit change in twist multiplier, which averages about 0.06 for the three yarns of Table I and the 81% maturity yarn of Table II for this range of twist. The 55% maturity cotton yarns show less change, but may be abnormal.

TABLE VI. EFFECT OF TWIST ON LUSTER OF YARN MERCERIZED AT ORIGINAL LENGTH

Yarn No.	Twist multiplier Nominal	Twist multiplier Found Singles	Twist multiplier Found Ply	Luster (contrast ratio) Unmercerized	Luster (contrast ratio) Mercerized	Change of luster per unit of TM* Unmercerized	Change of luster per unit of TM* Mercerized
36/2	3.0	2.73	2.85	1.61	2.01		
36/2	4.0	3.75	3.79	1.55	1.86	0.06	0.15
36/1	3.0	2.90		1.48	1.70		
36/1	4.0	3.75		1.43	1.54	0.05	0.19

* Based on twist found for singles. Twist was measured only in the original, unmercerized yarns.

Nominal versus *Actual Twist*

Tables I and II show the change of contrast ratio per unit twist multiplier both for nominal twist and for measured twist. Nominal twist is based on front-roll delivery speed and rate of spindle rotation. Actual twist was determined for the yarns of Table I and II, and was almost always found to be lower. Examples are given in Table VI. These yarns were intended to have the same twist multiplier in the singles and in the plying, the calculation for ply yarn being based on the equivalent singles. The same difference between actual and nominal twist is observed for both singles and ply, so the intended relation was obtained.

The reasons for the actual twist being lower than the nominal twist are not known with certainty. The effect of twist contraction at high twist multipliers would be to increase the turns per inch and decrease the count, both resulting in higher twist multiplier. The loss of twist in winding on is compensated by re-

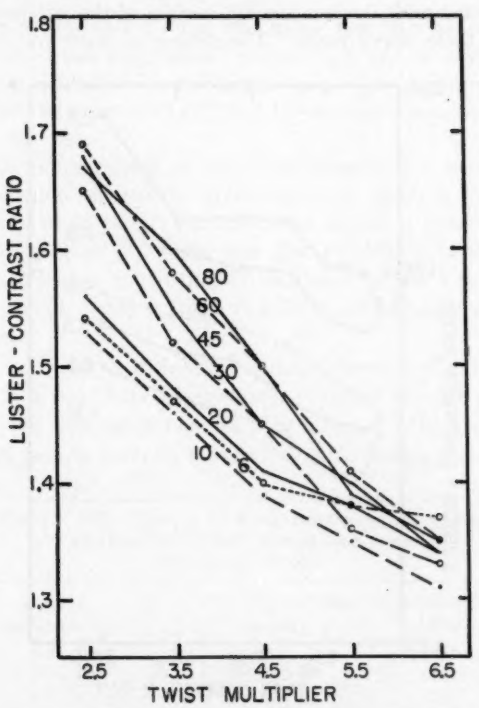


FIG. 4. *Effect of twist and yarn fineness in singles yarns all spun from the same cotton; luster plotted against twist multiplier.*

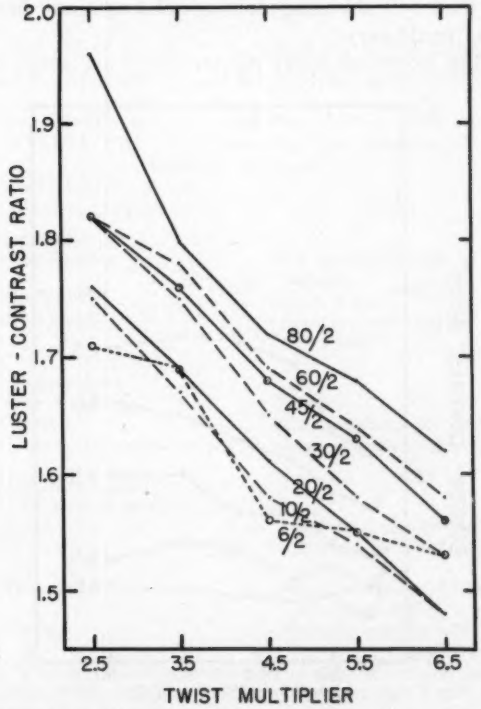


FIG. 5. *Effect of twist and yarn fineness in 2-ply yarns all spun from the same cotton; luster plotted against twist multiplier.*

moving the yarn over the end. Mechanical factors such as tape slippage, so that the spindle revolutions are less than nominal, may be involved.

Effect in Mercerized Cotton Yarns

Some of the yarns of the 81% maturity series were mercerized in the laboratory under tension at 100% of original length during mercerizing. The results given in Table VI show that the rate of change of luster with twist is much more rapid after mercerizing than for unmercerized yarns. Of course, this may be the result of greater effectiveness of mercerizing at lower twist.

Larger Range of Twist and Counts

A series of yarns varying from 2.5 to 6.5 in twist multiplier and from 6's to 80's in yarn number, all spun at S.R.R.L. from one lot of Wilds cotton, were examined. Yarns from three bobbins were measured, both as singles and 2-ply. This series is especially valuable because one kind of cotton was used throughout; in usual practice, different cottons would be used over this range, and staple length and fineness would vary.

The results of luster measurements are given in Figures 4 and 5. The ply twist was measured and found to be close to, but usually less than, the nominal twist. It was within 0.25 in all but three sets of yarns, so nominal twist is used for calculation of effect of change of twist on luster.

The plots of luster against twist show a nearly linear relation over this whole range of twist and counts, with a small indication of decreasing effect with increased twist in the higher range of twist. However, the average change of luster per unit change of twist multiplier over the whole range and for all yarn sizes is 0.066, which is in good agreement with the results in Tables I and II.

Effect of Yarn Fineness

Figures 4 and 5 show a tendency for the finer yarns to be higher in luster, a tendency also observed in the other series. The data have been replotted in Figures 6 and 7 to show the effect of yarn fineness at constant twist multiplier.

The observations on 6/1 and 6/2 yarns are out of the regular line of the others, which may be connected with the less smooth surface of the windings of these heavy yarns. The change of luster for the

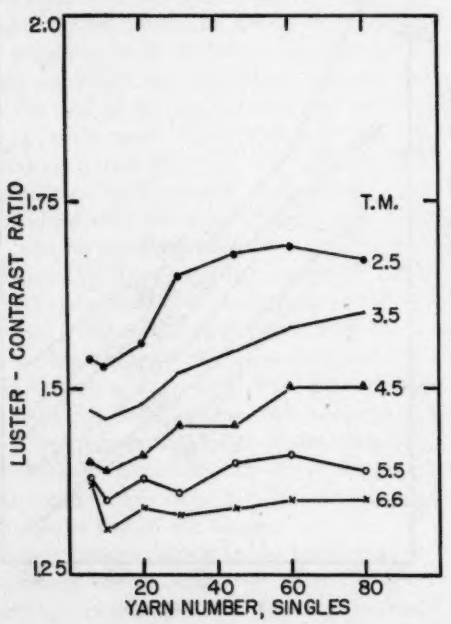


FIG. 6. *Luster plotted against yarn fineness for singles yarns spun from one kind of cotton.*

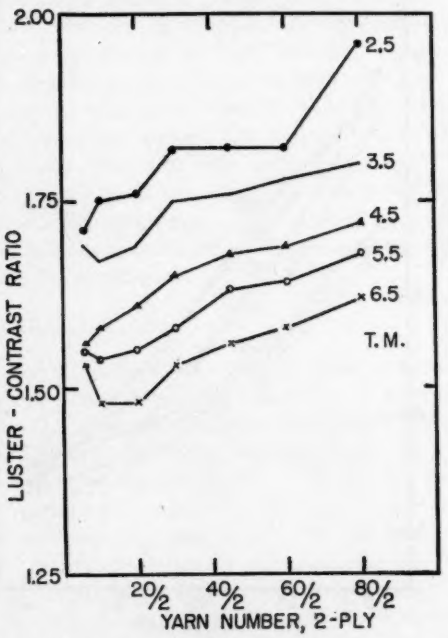


FIG. 7. *Luster plotted against yarn fineness for 2-ply yarns spun from one kind of cotton.*

most regular portion of the range of fineness—from 10's through 60's inclusive—is given in Table VII. In the singles yarns there seems to be an interaction between twist and the effect of yarn fineness, so that with less twist there is more effect of yarn fineness, but in 2-ply yarns the effect of yarn fineness is nearly constant at all levels of twist. As an average, the change of luster between 10's and 60's is 0.10 unit of contrast ratio. For ply yarns, and the middle range of twist in singles, the increase in contrast ratio is approximately proportional to the increase in yarn number, but this is clearly an empirical relation of limited range.

Effect of Plying

The effect of plying is much larger than the effect of twist or yarn fineness. It has been studied by Adderley and Oxley [1] with respect to the optimum relation between ply and singles twist for maximum luster. This was found to be

$$T_D = T_S/2^{0.5} = 0.7T_S = M \text{ (resultant count)}^{0.5},$$

where T_D and T_S are the turns per inch in the doubled and single yarns, respectively, and M is the twist multiplier for the singles yarn. The ply yarns of all the series spun at S.R.R.L. were spun according to this rule.

It is interesting to note that Schwarz [9] found the same relation for producing yarn which is balanced as to twist. An additional feature noticed in testing these ply yarns was that the length of the singles after untwisting is the same as the length of the ply—that is, that there is zero twist contraction.

In the series with Wilds cotton (shown in Figures 4, 5, 6, and 7) there is no distinct trend of the gain on plying with either twist or yarn fineness. The average gain in contrast ratio with plying in this series, which contains 35 pairs, is 0.21 unit. Including the data of Tables I, II, and III gives 59 pairs, in which the average is 0.20.

In mercerized yarns, only a limited number of comparisons of the same yarn—single and 2-ply—have been made, but the indication in Table VII is that the effect of plying is larger for mercerized yarn than for natural yarn.

TABLE VII. EFFECT OF YARN FINENESS ON LUSTER, AT CONSTANT TWIST, FOR RANGE FROM 10's THROUGH 60's

Twist multiplier	Increase of luster (contrast ratio) Singles	2-Ply
2.5	0.16	0.07
3.5	.12	.11
4.5	.11	.11
5.5	.06	.10
6.5	.04	.10

Summary and Comparison

Table VIII lists the various factors examined, and compares their relative effect on the luster of cotton. In comparison with mercerizing, which increases the contrast ratio by 0.7 to 0.8 unit or more in commercial plied yarn, all of these yarn structure effects are smaller, but still of importance because of the interaction between structure effects and the results of mercerizing. In order of degree of effect, the three most important factors are clean singeing, plying, and, where possible, decrease of twist.

Acknowledgment

The aid of Messrs. J. D. Dean, C. F. Goldthwait, and E. M. Buras, Jr., of the Cotton Chemical Proc-

TABLE VIII. COMPARISON OF YARN STRUCTURE EFFECTS ON LUSTER *

Structural property	Effect
From fibers:	
Fiber fineness	Not separated from other effects
Maturity	Small, if any
Fiber length	Small, increase 0.02 for 0.5 in. longer
From processing:	
Rate of carding	No effect
Combing	Small, increase 0.02 to 0.03
Singeing (for mercerized yarns)	Large, increase 0.40 to 0.60
Whole-yarn factors (in natural yarn) †	
Twist	Small, decrease 0.06 per unit increase in twist multiplier ‡
Fineness	Small, increase 0.10 from 10's through 60's
Plying	Medium, increase 0.20

* Change of luster is expressed in units of contrast ratio. In describing the effect, the range of twist is from 3 to 5, and counts from 10 to 60.

† In mercerized yarn, the effects are larger.

‡ The effect in mercerized yarn is about 3 times larger.

essing Division of the Southern Regional Research Laboratory, who advised and guided the project, and of Messrs. Louis Fiori, R. J. Cheatham, and J. J. Brown, of the Cotton Mechanical Processing Division, S.R.R.L., who furnished the specially spun yarns and discussed many questions of spinning practice, is gratefully acknowledged. We are also grateful to commercial spinners and mercerizers for experimental materials and production samples.

Dr. W. J. Hamburger of Fabric Research Laboratories made available a special series of acetate yarns, with data on fiber length distribution, and Messrs. Barker and Kerr of the Bureau of Plant Industries, U.S.D.A., made available yarns from the annual variety and environmental studies.

Literature Cited

1. Adderley, A., and Oxley, A. E., *J. Textile Inst.* **16**, T167–84 (1925).
2. Am. Soc. Testing Materials, "A.S.T.M. Standards on Textile Materials," Philadelphia, 1951.
3. Bureau of Plant Industry, U.S.D.A., "Annual Varietal and Environmental Study, 1950 Crop," mimeographed report, July 1951.
4. Federal Specification, Textile Test Methods, CCC–T–191B, U. S. Government Printing Office, 1951.
5. Fiori, L. A., and Brown, J. J., TEXTILE RESEARCH JOURNAL **21**, 750–7 (1951).
6. Merrill, G. R., Macormac, A. R., and Mauersberger, H. R., "American Cotton Handbook," 2nd ed., New York, Textile Book Publishers, 1949, p. 322.
7. Platt, M., TEXTILE RESEARCH JOURNAL **20**, 519–38 (1950).
8. Production and Marketing Administration, Cotton Branch, U.S.D.A., "Summary of Fiber and Spinning Test Results for Cotton Varieties Grown by Selected Cotton Improvement Groups, Crop of 1950," Washington, D. C., 1951.
9. Schwarz, E. R., TEXTILE RESEARCH **3**, 145–56 (1933).

(Manuscript received August 26, 1953.)

Investigations to Determine the Effects of the Washing Temperature and Time and the Concentration of the Washing Agents when Washing by Machine

Sigurd Köhler

Institutet för Tvätteknisk Forskning, Stockholm, Sweden

THE washing of textiles presents numerous chemical, physical, and technical problems, and the result is influenced by a number of different factors—*e.g.*, the nature of the water and the washing agents, the temperature and time schedule, and the concentrations of the washing agents.

As regards the water, it is the hardness which is of particular importance. This was pointed out long ago by Berzelius in his "Lärobok i Kemien" (Textbook of Chemistry), part IV, Stockholm, 1827, p. 371, and it is now generally recognized that the use of as soft a water as possible is a prerequisite for satisfactory washing results.

Even before the time of Berzelius, the washing agents, especially the chemical and physical properties of soap, were thoroughly investigated, and this is still being done. The results of these investigations largely expounded the chemical and physical properties of soap in aqueous solution, alone as well as together with alkalies. Although a great deal of knowledge concerning detergency has accumulated, a complete explanation of the action has not been given. For example, washing temperature, time, and the concentration of the washing agents are important factors which influence detergency. The effect of these factors on the durability of clothes and the general degree of whiteness obtained deserve consideration. In order to contribute to the elucidation of the effect of these three factors on the ordinary washing of white cotton and linen clothes, Institutet för Tvätteknisk Forskning (I.T.) (Institute of Textile Washing Research) carried out a series of investigations in 1947–1950, a summary of which is given here. The State Council of Technical Research contributed to the cost of this work.

Short reports with the results have previously been published once a year in the *Proceedings* of the Institute, Nos. 1–4, as they have been forthcoming.

A large number of papers dealing with the detergent action of soap solutions and the effect of washing on the strength of cotton and linen fabrics have been published. The following may be specially mentioned:

Rhodes and Brainard [5], Rhodes and Bascom [4], and Rhodes and Wynn [6], using laboratory apparatus for the washing, studied the effect on detergency of such factors as the temperature, time, soap concentration, pH value, and salts.

Madsen [1] showed that soaps of lauric and myristic acids at 100°C proved to have lower detergent effect than soaps of palmitic and stearic acids.

Morgan [2] studied the detergent action on sooted fabric. He used laboratory apparatus at 50°C and soap with different alkalies, and listed the alkalies in the following order with respect to their relative detergent action: Na_3SiO_3, NaOH, Na_3PO_4, and Na_2CO_3. For full-scale washing, the order was as follows: NaOH, Na_2CO_3, $Na_3H(CO_3)_2$, Na_2SiO_3, and Na_3PO_4.

Norlin and Skärblom [3] found that, *inter alia*, soaps containing highly unsaturated fatty acids may greatly reduce the strength of cotton and linen fabrics due to an autoxidation of the fatty acids during the drying of the fabrics.

Schnyder [7] carried out extensive investigations into the effect of washing and bleaching processes on cotton and linen fabrics. As regards bleaching agents, he stated that peroxide bleaching is simpler than chlorine bleaching. At the same degree of bleaching, however, the former causes more damage to the fibers.

Vaughn and Vittone [9] studied the detergent action of soaps and several builders at 60°C, and classified the builders with respect to detergency and whiteness retention for the conditions used.

Utermohlen and Ryan [8] compared chemical and photometric measurements for the determination of

the effects of washing procedures on soiled cloth. They found that iron oxide-removal values calculated by the linear method from reflectance data did not agree either with the values calculated from reflectance data by the use of the Kubelka-Munk equation nor with the absolute values obtained by analyses for iron.

The Washing Process and the Water

Customary procedure in Sweden in machine washing, particularly as concerns hospital linen, comprises three main operations—*viz.*, soaking, washing, and rinsing.

Soaking involves treating the clothes with water, normally about 8 liters per kg. dry weight, for about 10 min. When the water is drawn off, about 5½ liters runs out and about 2½ liters per kg. wash goods is retained by the clothes. Some operators add a small amount of alkali to the soaking water to increase the effect of the soaking. If the clothes are very dirty, they are sometimes soaked in several changes of water.

When washing, a small quantity of water—about 1½ liters per kg. clothes—is added together with soap and, in most cases, alkali, the liquor then being heated to the maximum temperature desired—for white wash, generally 80°C or more. This temperature is maintained for 5 to 10 min. or longer, after which the wash liquor is drawn off. Several washes are often used for very dirty clothes, the maximum temperature being increased for each new wash.

After the washing is the rinsing. As a rule, a fairly small quantity of water is added for the first rinse, the quantity being increased for subsequent rinses. The number of rinses is usually five or more.

The total water consumption for the whole washing process is generally 30–40 liters per kg. clothes, but often considerably more.

Water-soluble impurities in the clothes—*e.g.*, sugar, urine, blood, sweat, etc.—are dissolved in the soaking water, and some insoluble substances are loosened and suspended in the water. Oils and fats are not soluble in water and have, moreover, distinctly water-repelling properties. Like other substances which are not soluble in water, they cannot be removed from the clothes by means of water alone.

Soap, usually together with alkali, is added to the water when washing. The soap reduces the surface tension of the water and also the interfacial tension to oils and fats and other impurities and to textile fibers. Since soap also has emulsifying and peptizing properties, fats, oils, and other impurities, which are not soluble in the wash liquor, are to a large extent loosened from the clothes and dispersed in the solution. This process is assisted by the temperature increase and the mechanical action in the washing machine. The addition of alkali serves to increase the pH value of the solution and to neutralize the acid components of the dirt. Increased alkalinity also makes certain impurities soluble in the wash liquor—*e.g.*, fatty acids, some albumins, vegetable dyes (berry dyes), etc.

The object of the rinse is to remove the wash liquor from the clothes together with dissolved and dispersed dirt. For several reasons it is advisable to begin rinsing with a relatively small quantity of water. Should the wash liquor be diluted too much at the first rinse, there is the risk that part of the dispersed dirt will be reprecipitated on the clothes, which may easily result in poor whiteness.

Obviously, the water plays an important part in the washing process. To some extent, the washing results are dependent upon the nature of the water. Ordinary water is far from pure. It always contains dissolved substances of various kinds. To be suitable for use as wash water, it should be satisfactory from a hygienic point of view, practically colorless, and as free as possible from calcium and magnesium salts as well as iron and manganese compounds. Calcium and magnesium (water hardeners) as well as iron and manganese combine with soap and alkali to produce compounds which are difficult to dissolve in water and parts of which are precipitated on the clothes, which acquire a more or less pronounced grey or greyish yellow tinge. The discoloration is usually increased with the number of washes, and the fabric becomes greasy and often stiff to the touch.

The amount of soap consumed as regards the hardness is proportional to the degree of hardness (about 0.1 g. fatty acid per liter and degree of hardness; 1 German degree of hardness (°dH) = 10 mg. CaO per liter). If an amount of soap corresponding to 1 g. fatty acid per liter water of 10°dH is added, the whole amount is accordingly precipitated by the hardeners. An amount of soap corresponding to 1 g. fatty acid per liter water is often quite sufficient for washing in water that is practically free from calcium and magnesium compounds. Washing in hard water consequently involves an increased consumption of

soap, but even if sufficient soap is used, the result is poorer than that obtained with soft water.

For the above reasons it is of great importance that the water used for washing be soft and practically free from iron and manganese. The hardness should in any case be less than 1°dH, the iron content less than 0.1 mg./liter, and the manganese content less than 0.05 mg./liter.

Hard water can be softened by means of a base-exchange filter. Iron and manganese can also be removed, usually through oxidation and filtration.

The Washing Procedure Used in the I.T. Investigations

All washing tests were carried out in two identical washing machines of stainless steel in the laundry of a Stockholm hospital. The diameter of the cage of the machines was 85 cm. and the length 160 cm. The cage was provided with three ribs, each 15 cm. high and 9 cm. wide at the base. The total volume of the cage was 870 liters. For the washing tests the machine was charged with 70 kg. clothes. The volume was thus 12.4 liters per kg. of goods. Occasional tests with other loads were also made. The washing liquor in the machines was heated by means of direct steam. The machines were equipped with thermometers, which were checked often.

Softened Stockholm water was used for the tests. The water was softened by means of base-exchange filters (Wofatit). The hardness of the softened water averaged 4–6 mg. CaO per liter (0.4°–0.6°dH). The water put into the machine was measured by means of a water meter connected to the main. The following quantities were added in the course of the different operations:

	Total quantity (liters)	Quantity per kg. wash goods (liters)
Soaking	560	8.0
Washing	105	1.5
First rinse	105	1.5
Second rinse	210	3.0
Third rinse	420	6.0
Fourth rinse	420	6.0
Fifth rinse	420	6.0
Total	2,240	32.0

During or after the last rinse, 45 ml. glacial acetic acid was added as a sour.

The various time-temperature schedules used are shown in Figure 1.

When not otherwise stated, soap of fatty acids with a titer of about 40°C and iodine value 46–60 was used for the washing tests.

The washing tests were performed by Mr. S. Backholm of the Institute.

The Effect of Maximum Temperature, Time at Maximum Temperature, and Concentration of Washing Agents on the Detergent Action

Soiled clothes contain impurities of widely differing kinds. The following types may be differentiated with regard to the reaction of the dirt to water and washing agents in aqueous solutions: (*a*) substances which are more or less easily soluble in water or wash liquor and which are removed from the fabric and dissolved in the solution in the course of the washing process; (*b*) substances which are insoluble in water and wash liquor, but which can be detached from the fabric and dispersed in the liquor or water; (*c*) impurities which are neither soluble nor dispersible in water or wash liquor. Type *a* includes many organic substances—*e.g.*, certain proteins, urine, blood, sweat components, etc.—and certain elements of food and beverages—*e.g.*, various kinds of sugar, starch, many dyes, and free fatty acids—which are dissolved after saponification by the washing alkali, etc. Type *b* includes soot, fats, oils, minerals, fibrous matter, etc. Type *c* includes such substances as rust, silver, mercury, lead, and copper stains, certain dyes, certain coagulated proteins, etc., for the removal of which special treatment is required (bleaching or some other treatment). It must be pointed out that this classification of dirt into different types is purely schematic. Each group contains dirt which is more or less easily soluble or dispersible and which should rightly be classified between two types.

It is not possible to evaluate the relative detergent effect of various washing procedures satisfactorily by washing ordinary soiled clothes. This is due, *inter alia*, to the difficulty of measuring or determining the relative degree of cleanness of washed clothes, particularly if the differences are slight, and to the impossibility of getting identically soiled clothes from case to case. It must also be remembered that even if both of two washing methods give practically clean clothes, it does not necessarily follow that the two methods have the same detergent effect. It is necessary to use a fabric which is so heavily soiled that it will not become clean in either case, only showing

a higher degree of cleanness (whiteness) the more effective the washing method. Therefore, a fabric is generally used which has been purposely soiled or stained with suitable agents. These soiling agents should be such that the change in the whiteness of the fabric accomplished by the washing may be determined by sufficiently simple and quick methods. The change in the whiteness of the fabric is generally measured for this purpose. This procedure is quite like that used in practice. After all, the cleanness of washed goods is primarily judged by sight. The use of the degree of whiteness as a measure of the detergent effect presupposes that the artificial dirt is colored and also that it consists of a homogeneous substance. If the soiling agent contains two or more dye components, it is quite conceivable that one washing method would result in increased whiteness due to the removal of mainly one of the components, while another method would remove mainly the other one, but that in both cases the same degree of whiteness would be obtained. It would then be concluded that the two methods have the same detergent effect, which might be misleading. A direct determination of the respective proportions of the two dyes would in fact be required to allow correct evaluation of the washing results. For this reason, the use of a composite soiling agent, corresponding to the average composition of the dirt found on wash goods, is not suitable for comparative studies of the detergent effect of different washing methods. Colloidal indigo (Heermann), soot with different admixtures (Götte, Rhodes and Wynn, Rhodes and Bascom, Morgan, and others), and ultramarine (Madsen) are some of the soiling agents which have been used for the above purpose.

As early as in the middle of the 1920's The Government Testing Institute of Sweden made comparative determinations of the detergent effect of different washing methods. For this purpose they used fabrics stained with soot with or without oil, cocoa in milk, claret, and stains of blood, vegetable dyes, etc. After various tests I.T. found the following three dyes suitable—*viz.*, soot + tallow + paraffin oil, ultramarine, and claret. The staining method used was the one outlined by Morgan [2], among others. A strip of cotton fabric is drawn through the dye bath. The strip used for the I.T. tests was 2 dm. wide and about 8 m. long. It is led from the bath between the rollers of a wringing machine and then back to the bath via a series of rollers. For the staining process, the ends of the strip are sewn together so that an endless band is formed, which is drawn through the bath by the wringing machine a given number of times. The soot is dispersed in a solution of tallow and paraffin oil in carbon tetrachloride, 2 g. of carbon black of the quality used in the manufacture of carbon paper being added to each liter of carbon tetrachloride solution. The ultramarine (20 g./liter) is dispersed in water to which a wetting agent has been added (0.5 g. Nekal BX Trocken per liter of water). The ultramarine band is rinsed in water in the dyeing machine after the staining. Different brands of cheap claret have been used, since it has proved impossible to obtain the same brand always.

It has been known for some time that the age of a claret stain has bearing on its resistance to wash-

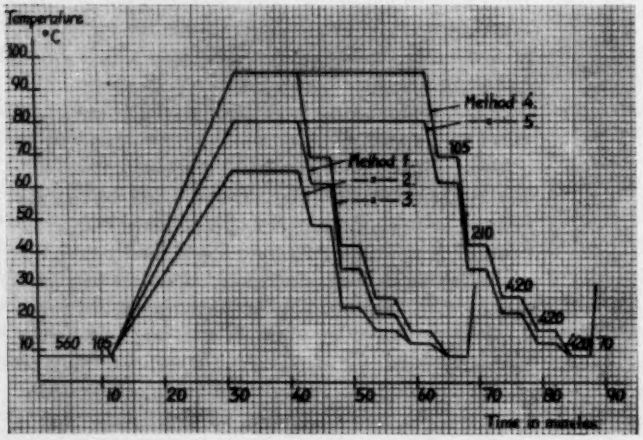


FIG. 1. *Temperature-time schemes used in I.T. investigations.*

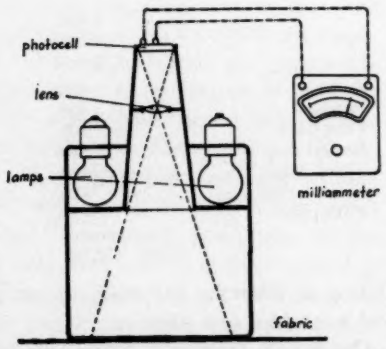


FIG. 2. *Schematic view of the whiteness measuring equipment.*

ing. The first wash of each test series was therefore always carried out within the shortest possible period (2 to 3 days), and the stain was generally about 2 weeks old. Each stained band provided 32 strips of fabric of about 2 dm. × 2 dm., which were distributed over eight washing series—*i.e.*, four strips for each series.

The staining of different bands stained with the same agent often turned out differently, resulting in different degrees of whiteness before and after the wash. For the sake of comparison, stained strips from each band were therefore always washed according to a standard method (method *1*, Figure 1) with soap corresponding to 4 g. of fatty acid and 1 g. of NaOH per kg. wash goods. The whiteness of the remaining strips of fabric from the same band, washed according to other methods or with other washing agents, is given as a percentage of the whiteness of the strips washed according to the standard method.

The total reflection of light from the strips of fabric, measured by means of a photocell, serves as a measure of the degree of whiteness. The apparatus used for this purpose was constructed at The Government Testing Institute by Mr. H. Axelson. An area with a diameter of 18 cm. may be measured in the apparatus. Each strip of fabric was measured on both sides, the other three strips with the same staining serving as a bottom layer. The whiteness of a plate coated with magnesium oxide is designated 100. The plate (a white-lacquered aluminum plate) was coated with magnesium oxide deposited from a burning magnesium band to a thickness of at least 1 mm. A gypsum plate, made of about 80% calcined gypsum and about 20% titanium white, the whiteness of which was about 90% compared with magnesium oxide, was used as a working standard. The surface of this plate can be renewed by scraping. Since only one photocell had been used so far, electric current from a storage battery was used for the light emission in the apparatus. The adjustment to the working standard was checked between each measuring. The photocell used for most of the measurings was adjusted by means of filters so that its sensitivity roughly corresponded to that of the human eye. Such adjustment, however, proved unnecessary, since the same results were obtained with an unadjusted photocell. Figure 2 shows a sketch of the apparatus. The glass lens of the apparatus projects a picture of the measuring surface on the surface of the photocell. Because of the relatively large measuring surface, it is possible to gage the average whiteness of the strip of fabric. This is very important, since the color of the washed strips of fabric stained with soot or ultramarine is often more or less uneven.

Four strips of fabric of each color were used for each test, each piece being measured on both sides. The deviation from the averages obtained through repeated measuring of four strips was normally less than 0.5. The pointer galvanometer used is graded into 100 parts, 0 indicating complete blackness and 100 the whiteness of the magnesium oxide plate. The value read from the galvanometer scale gives the whiteness (light reflection) of the piece of fabric as a percentage of the whiteness of magnesium oxide.

The soiled pieces of fabric—twelve for each test (four of each color)—were always washed three times according to each method, their relative whiteness being determined after one and three washes, and in some cases also after two washes.

Table I shows that, with regard to the soot- and ultramarine-stained strips of fabric, the spread of the individual values is the most pronounced after the first wash and the least pronounced after the third. This is, of course, to be expected, since all of the strips should approach the same degree of whiteness after repeated washings. The equalization due to the fact that a strip of fabric which has attained a relatively low degree of whiteness in the first wash increases its whiteness to a relatively greater extent through subsequent washes must also be taken into account. The increase of whiteness per wash is usually comparatively large after the first wash, smaller after the second, and still smaller after the third. The data of Table II may be cited as an example.

The figures given under 1 in Table II indicate the difference between the whiteness values (%) after and before the first wash, under 2 the difference between the whiteness after the second and the first washes, and under 3 between the whiteness after the third and the second washes. Before the washing, the whiteness of the soot-stained fabric was 13%, that of the ultramarine-stained 37%, and that of the claret-stained 62%. The figures in Table II show that the increase of whiteness of soot-stained fabric was 3.88, that of ultramarine-stained fabric 3.83, and that of claret-stained fabric 3.55 times greater after the first than after the second wash; and for soot-stained fabric 2.28, for ultramarine-stained fabric 1.84, and for claret-stained fabric 1.76 times greater after the second than after the third wash.

All the washings were carried out in softened

TABLE I. THE VARIANCE (s^2) IN THE WHITENESS VALUES AFTER 1, 2, AND 3 WASHES ACCORDING TO DIFFERENT METHODS (SOAP CORRESPONDING TO 4 G. FATTY ACID USED FOR ALL TESTS)

			Fabric stained with:								
			Soot			Ultramarine			Claret		
	No. of washes →		1	2	3	1	2	3	1	2	3
Alkali	Max. temp. (°C)	Time at max. temp. (min.)									
Series 19											
1 g. NaOH	80	10	21.5	5.8	4.1	14.6	2.0	1.4	2.5	3.7	3.4
1 g. NaOH	80	10	6.9	2.2	1.7	1.5	0.9	0.8	0.8	1.7	1.1
3 g. $Na_2SiO_3 \cdot 5H_2O$	80	2	11.8	8.0	3.8	8.1	3.1	1.8	4.7	1.1	1.6
3 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	9.8	4.9	1.4	5.2	1.2	1.2	0.7	1.9	1.5
3 g. $Na_2SiO_3 \cdot 5H_2O$	80	30	5.6	1.9	0.7	2.4	3.2	2.4	1.8	1.0	1.3
3 g. $Na_2SiO_3 \cdot 5H_2O$	65	10	10.2	1.7	2.5	8.2	0.8	0.6	1.9	1.2	1.4
3 g. $Na_2SiO_3 \cdot 5H_2O$	95	10	7.2	3.6	1.7	7.6	2.2	1.0	3.8	3.2	2.5
Series 20											
1 g. NaOH	80	10	5.9	3.5	3.5	5.0	0.4	0.3	1.1	2.0	0.5
1 g. NaOH	80	10	4.6	4.6	2.5	2.9	0.8	0.4	0.2	0.4	0.9
1 g. NaOH *	80	10	3.9	6.3	3.7	0.8	0.3	0.6	0.3	0.4	0.5
1 g. NaOH †	80	10	2.0	1.8	3.2	5.0	1.4	0.5	0.5	0.3	0.2
1 g. NaOH ‡	80	10	3.3	2.4	2.1	1.3	0.0	0.1	0.8	0.7	0.1
None	80	10	22.0	5.4	5.5	2.9	0.5	0.8	0.7	0.4	0.1
1 g. NaOH **	80	10	2.0	2.4	2.1	3.1	1.1	0.1	0.7	0.7	0.1
1 g. NaOH §	80	10	6.2	2.9	1.4	3.3	2.7	0.8	2.5	1.7	0.4
		Average	8.19	3.83	2.66	4.79	1.37	0.85	1.53	1.36	1.04

* NaOH added 10 min. after the soap.
† Soap added 10 min. after the NaOH.
‡ Soap and NaOH dissolved and added at the same time.
** 50 kg. wash goods in the machine.
§ 90 kg. wash goods in the machine.

TABLE II. INCREASE OF WHITENESS PER WASH (AVERAGES OF 8 TESTS IN SERIES *19*)

				Fabric stained with:					
		Soot			Ultramarine			Claret	
Wash No. →	1	2	3	1	2	3	1	2	3
Gradual increase of whiteness	44.5	10.7	4.9	26.8	7.1	3.8	9.5	2.7	1.8

TABLE III. WHITENESS OF STAINED PIECES OF FABRIC, WASHED 3 TIMES IN THE SAME WAY AND AT THE SAME TIME

Test	No. of individual values		Fabric stained with: Soot	Ultramarine	Claret
21A	(14)16	Whiteness (%)	(14)57.3	80.3	70.3
		Variance	1.6	0.97	0.85
21B	8	Whiteness (%)	57.0	80.4	71.3
		Variance	3.38	0.15	0.47
21C	8	Whiteness (%)	56.9	80.8	70.3
		Variance	3.31	0.12	0.44
21E	8	Whiteness (%)	54.4	80.5	68.4
		Variance	2.96	0.81	0.29

water, and the results are therefore, strictly speaking, only applicable when practically soft water is used. Also, the object of the investigation was only to give a survey of the effects of the temperature, the time, and the concentration of the washing agents on the detergent action. Detailed studies are required for further elucidation of relevant points, including studies of the test methods. In the course of the work there were in some cases certain discrepancies in the results obtained from repeated tests according to the same washing method, the cause of which should be investigated further. The data given in Table III may be cited as an example. They were obtained for pieces of fabric from the same band which had been washed at least three times. Soap corresponding to 4 g. of fatty acid and 1 g. NaOH and the temperature-time schedule 80°C, 10 min. (see Figure 1), were used for the washing tests.

TABLE IV. RESULTS OF 3 SERIES OF DETERMINATIONS OF THE RELATIVE DETERGENT ACTION WHEN WASHING WITH SOAP CORRESPONDING TO 4 G. FATTY ACID AND DIFFERENT AMOUNTS OF NaOH *

Amount of NaOH (g.)	Relative degree of whiteness after 3 washes for fabrics stained with: Soot a	b	c	Mean value	Ultramarine a	b	c	Mean value	Claret a	b	c	Mean value
0.5	105	99	103	103	95	98	97	97	102	104	97	101
4.0	96	100	100	98	110	104	99	104	112	108	115	111

* Maximum temperature, 80°C; total washing time, 30 min., 10 min. of which was at maximum temperature.

TABLE V. RESULTS OF 2 SERIES OF DETERMINATIONS OF THE RELATIVE DETERGENT ACTION WHEN WASHING AT DIFFERENT MAXIMUM TEMPERATURES *

Max. temp. (°C)	Relative degree of whiteness after 3 washes for fabrics stained with: Soot a	b	Mean value	Ultramarine a	b	Mean value	Claret a	b	Mean value
65	99	99	99	99	98	99	99	92	95
90	104	104	104	108	106	107	100	105	103

* Total washing time, 30 min., 10 min. of which was at maximum temperature; washing agent, soap corresponding to 4 g. of fatty acid and 1 g. NaOH.

TABLE VI. RESULTS OF 3 SERIES OF DETERMINATIONS OF THE RELATIVE DETERGENT ACTION WHEN WASHING WITH DIFFERENT SOAP CONCENTRATIONS AND 1 G. NaOH *

Soap conc. corresponding to:	Relative degree of whiteness after 3 washes for fabrics stained with: Soot a	b	c	Mean value	Ultramarine a	b	c	Mean value	Claret a	b	c	Mean value
2 g. fatty acid	103	102	—	102	105	103	—	104	98	95	—	97
8 g. fatty acid	98	103	104	102	—	101	101	101	104	98	103	102

* Total washing time, 30 min., 10 min. of which was at maximum temperature (80°C).

TABLE VII. RESULTS OF 4 SERIES OF DETERMINATIONS OF THE RELATIVE DETERGENT ACTION WHEN WASHING WITH SOAP CORRESPONDING TO 4 G. FATTY ACID AND 3 G. $Na_2SiO_3 \cdot 5H_2O$ *

Total washing time (min.)	Time at max. temp. (min.)	Relative degree of whiteness after 3 washes for fabrics stained with: Soot a	b	c	d	Mean value	Ultramarine a	b	c	d	Mean value	Claret a	b	c	d	Mean value
22	2	99	91	97	—	96	94	85	97	—	92	97	98	99	—	98
30	10	100	93	104	99	99	94	87	101	98	97	99	101	101	104	101
50	30	105	107	111	—	108	100	100	104	—	101	104	106	106	—	105

* Maximum temperature, 80°C. The total washing time and the time at maximum temperature differed.

Test 21E in Table III shows a significant divergence in the whiteness of soot-stained and claret-stained fabric as compared with the other tests. When making practical washing tests under fairly crude test conditions, a relatively large variation of the results of repeated tests according to the same washing method might, of course, be expected. It would, however, be reasonable to expect that the differently stained pieces of fabric which are washed together should be similarly affected under various test conditions. This, however, is far from the case, as may be seen from Tables IV–VII. Because of this variation, one should not attach too much importance to the individual values, even though most of them are the average values of the results of two to four tests.

If the degree of whiteness is calculated as a percentage of that of the pieces of fabric washed according to the standard method after 1, 2, and 3 washes, this relative whiteness turns out to be nearly the same after 1, 2, and 3 washes (see Table VIII).

It should therefore be correct to base the evaluation on the mean value of the relative whiteness after 1, 2, and 3 washes. After the third wash the variations are, however, generally considerably smaller than after the first or even the second wash, particularly with regard to the fabrics stained with soot and ultramarine (see Table I). In the results reported in Tables IX–XI, the relative degree of whiteness after the third wash was therefore used as a basis for evaluating the detergent effect. The amounts of soap and alkali given in the tables were calculated per kg. of air-dry wash goods in the washing machine.

Of the results shown in Table VIII, the last two deserve special attention since they confirm the observation that a large amount of clothes in the machine gives a poorer detergent effect than a small amount. However, this only applies to dirt of the soot and ultramarine type, or, in other words, the kind of dirt for which mechanical action is of primary importance.

The data reported in Tables IX–XI are shown in Figures 3–6.

Effect of the Temperature

When washing with soap and alkali, an increase of the temperature within the range of 65°C to 95°C, all other factors being equal, results in an improvement of the detergent effect on all three types of dirt. This improvement is roughly proportional to the temperature increase.

It should be pointed out, however, that the washing tests with 4 g. NaOH at 80°C, and at 95°C, gave

TABLE VIII. WHITENESS AFTER 1, 2, AND 3 WASHES ACCORDING TO DIFFERENT METHODS, IN % OF THE WHITENESS OF FABRIC WASHED PARALLELLY ACCORDING TO THE STANDARD METHOD

Conc. of washing agents per kg. wash goods				Fabric stained with:								
				Soot			Ultramarine			Claret		
Soap corr. to fatty acid (g.)	Alkali	Max. temp. (°C)	Time at max. temp. (min.)	1	2	3	1	2	3	1	2	3
4	3 g. $Na_2SiO_3 \cdot 5H_2O$	80	2	93.4	97.6	99.0	94.8	94.2	94.1	99.3	98.0	97.2
4	3 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	98.4	97.9	99.7	91.2	92.2	93.5	99.0	97.7	99.1
4	3 g. $Na_2SiO_3 \cdot 5H_2O$	80	30	108.0	104.3	104.5	101.2	100.4	100.0	103.5	102.7	103.9
4	3 g. $Na_2SiO_3 \cdot 5H_2O$	65	10	103.9	99.3	101.5	94.3	94.7	94.3	98.7	99.1	98.7
4	3 g. $Na_2SiO_3 \cdot 5H_2O$	95	10	104.6	102.5	105.3	96.8	97.1	98.9	102.3	101.2	103.3
8	1 g. NaOH	80	10	107.8	104.7	104.2	101.2	101.2	101.1	103.7	102.0	102.7
4*	1 g. NaOH	80	10	98.8	101.9	102.2	104.5	101.8	101.2	104.3	103.8	102.6
4†	1 g. NaOH	80	10	95.0	94.1	93.9	97.9	97.3	97.7	99.4	98.0	98.2
4‡	1 g. NaOH	80	10	102.5	98.6	101.9	104.5	101.9	100.9	101.9	99.9	100.1
4	none	80	10	91.6	95.7	98.7	98.6	96.3	95.4	107.7	105.6	102.8
4**	1 g. NaOH	80	10	107.7	102.6	102.8	103.6	101.3	101.2	103.7	99.5	99.7
4§	1 g. NaOH	80	10	95.7	98.8	98.3	93.4	94.8	95.6	93.9	98.9	99.6
		Average		100.6	99.8	101.0	98.5	97.8	97.8	101.5	100.5	100.7

* NaOH added 10 min. after the soap.
† Soap added 10 min. after the NaOH.
‡ Soap and NaOH dissolved and added at the same time.
** 50 kg. wash goods in the machine.
§ 90 kg. wash goods in the machine.

TABLE IX. EFFECT OF THE MAXIMUM TEMPERATURE ON THE DETERGENT ACTION

A. Soap concentration corresponding to 4 g. fatty acid (total washing time, 30 min., 10 min. of which was at maximum temperature)

Max. temp. (°C)	Without alkali	Relative degree of whiteness after 3 washes with soap and: NaOH 1 g.	NaOH 4 g.	$Na_2SiO_3 \cdot 5H_2O$ 3 g.	$Na_3PO_4 \cdot 12H_2O$ 4 g.	Na_2CO_3 3 g.	Na_2CO_3 9 g.	$Na_3H(CO_3)_2 \cdot 2H_2O$ 5 g.	Mean value
Soot-stained fabric									
65	91	99	94	95	94	89	94	94	94
80	95	100	98	99	99	99	95	95	98
95	99	103	98	108	104	108	104	100	103
Ultramarine-stained fabric									
65	97	99	97	94	88	94	97	84	94
80	101	100	104	97	97	93	96	84	96
95	100	105	119	97	99	114	109	102	105
Claret-stained fabric									
65	109	95	104	97	97	95	97	95	98
80	112	100	112	101	103	97	102	100	103
95	109	104	121	104	106	103	112	103	108

B. Soap concentration corresponding to 4 g. fatty acid and 4 g. NaOH (total washing time, 50 min., 30 min. of which was at maximum temperature)

Max. temp. (°C)	Relative degree of whiteness after 3 washes for fabrics stained with: Soot	Ultramarine	Claret
80	103	130	120
95	108	140	124

TABLE X. EFFECT OF THE TIME AT MAXIMUM TEMPERATURE ON THE DETERGENT ACTION *

Max. temp. (°C)	Time at max. temp. (min.)	Relative degree of whiteness after 3 washes with soap and: NaOH 1 g.	NaOH 4 g.	$Na_2SiO_3 \cdot 5H_2O$ 3 g.	$Na_3PO_4 \cdot 12H_2O$ 4 g.	Na_2CO_3 9 g.	Mean value
Soot-stained fabric							
80	2	98	89	96	92	94	94
80	10	100	98	99	100	95	98
80	30	104	103	108	107	105	105
95	10	—	99				
95	30	—	108				
Ultramarine-strained fabric							
80	2	95	95	92	81	98	92
80	10	100	104	97	96	95	98
80	30	107	130	101	102	109	110
95	10	—	126				
95	30	—	140				
Claret-stained fabric							
80	2	96	104	98	97	98	99
80	10	100	111	101	99	102	103
80	30	105	120	105	104	113	109
95	10	—	121				
95	30	—	124				

* Soap corresponding to 4 g. fatty acid was used in all the washing tests. Heating time to maximum temperature, 20 min.

practically the same degree of whiteness on soot-stained fabric. Other alkalies, even at sufficiently high concentrations, weaken the detergent effect on soot-stained fabric. The use of high alkali concentrations or a simultaneous increase of the alkali concentration and the temperature may consequently result in the temperature increase having little or no effect on the degree of whiteness obtained on fabric soiled with soot.

In some washing tests with low-titer soap an increase of the temperature had the same effect as when high-titer soap was used. These tests, however, were not sufficiently extensive to warrant any conclusions.

Effect of the Time at Maximum Temperature

A prolongation of the time at maximum temperature, other factors being equal, results in a general increase of the detergent action. This increase is practically proportional to the time, if the latter is prolonged from 2 to 30 min.

Effect of the Concentrations of the Washing Agents

Soap concentration.—Washing tests were carried out with soap concentrations corresponding to from 1 to 8 g. fatty acid together with 1 g. NaOH per kg. wash goods. The maximum temperature was 80°C and the total washing time 30 min., 10 min. of which was at maximum temperature. The results showed that under these conditions the detergent action was practically the same whether the soap concentration corresponded to 2 g., 4 g., or 8 g. fatty acid. If the concentration of fatty acid was reduced to 1 g., the detergent effect was decreased. Repeated tests with such a low concentration of soap gave very different values, probably because of the varying dirt content of the clothes washed together with the test pieces.

These results appear to indicate that the use of more soap than that required for the dispersion of the dirt is a means of increasing the washing costs, but not a means of increasing the detergent effect. A distinct lathering of the wash liquor is usually a sign that the soap concentration is adequate. If the

TABLE XI. EFFECT OF THE CONCENTRATION OF WASHING AGENTS ON THE DETERGENT ACTION

A. Soap concentration *

Amount of soap per kg. wash goods (fatty acid, g.)	Relative degree of whiteness after 3 washes with soap and 1 g. NaOH for fabrics stained with: Soot	Ultramarine	Claret	Mean value
1	92	102	96	97
2	102	104	97	101
4	100	100	100	100
8	102	101	101	101

B. Alkali concentration †

NaOH			$Na_2SiO_3 \cdot 5H_2O$			$Na_3PO_4 \cdot 12H_2O$			Na_2CO_3			
			Relative degree of whiteness after 3 washes with:									
(g.)	pH	Whiteness	(g.)	pH	Whiteness	(g.)	pH	Whiteness	(g.)	pH	80°C whiteness	95°C whiteness
Soot-stained fabric												
0.5	8.9	103	1.5	10.4	97	1.0	9.9	104	3.0	10.2	99	108
1.0	11.0	100	3.0	11.0	99	4.0	10.6	100	9.0	10.5	95	104
4.0	12.1	98	10.0	11.9	98	8.0	11.1	100	18.0	10.9	87	96
Ultramarine-stained fabric												
0.5		97	1.5		98	1.0		94	3.0		93	114
1.0		100	3.0		97	4.0		96	9.0		95	109
4.0		104	10.0		99	8.0		96	18.0		90	106
Claret-stained fabric												
0.5		101	1.5		101	1.0		101	3.0		97	103
1.0		100	3.0		101	4.0		99	9.0		102	112
4.0		111	10.0		115	8.0		106	18.0		102	112

* Maximum temperature, 80°C; total washing time, 30 min., 10 min. of which was at maximum temperature.

† Soap corresponding to 4 g. fatty acid. Maximum temperature, 80°C (when using Na_2CO_3, also 95°C); total washing time, 30 min., 10 min. of which was at maximum temperature.

lathering is so strong that the lather flows out of the washing machine, it is an indication that the soap concentration is unnecessarily high.

Alkali concentration.—0.5–4.0 g. NaOH, 1.5–10.0 g. $Na_2SiO_3 \cdot 5H_2O$, 1–8 g. $Na_3PO_4 \cdot 12H_2O$, and 3–18 g. Na_2CO_3 were used for the washing tests. The same soap concentration, corresponding to 4 g. of fatty acid per kg. of clothes, was used throughout. The maximum temperature was 80°C (when Na_2CO_3 was used, also 95°C) and the total washing time 30 min., 10 min. of which was at maximum temperature. The results show that the whiteness of the soot-stained fabric generally decreased a little when the alkali concentration was increased. The whiteness of the ultramarine-stained fabric did not appear to have been appreciably affected by variations in the alkali concentration within the limits fixed for the purpose of these tests. When NaOH was used, the whiteness increased with concentration, while the situation was the reverse when Na_2CO_3 was used. A change in the concentration of metasilicate and triphosphate, respectively, had practically no effect on the whiteness of the ultramarine-stained fabric. The whiteness of the claret-stained fabric was definitely more pronounced at the higher than at the lower alkali concentrations.

Only where a special type of impurity (the claret type) is concerned does an increase of the alkali concentration over and above about 0.025 mol per kg. of wash goods (about 1 g. NaOH, about 5 g. $Na_2SiO_3 \cdot 5H_2O$, and about 3 g. Na_2CO_3) result in an increase of the detergent action of the wash, the strong alkalies, NaOH and Na_2SiO_3, having proved the most effective in this respect. An increase of

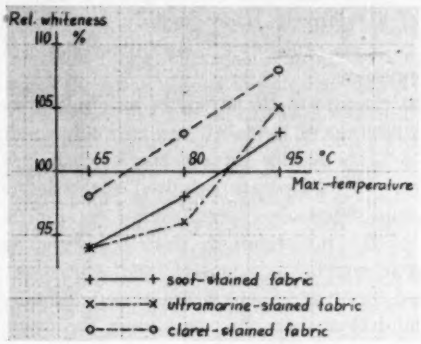


FIG. 3. *Influence of maximum temperature on the detergent action.*

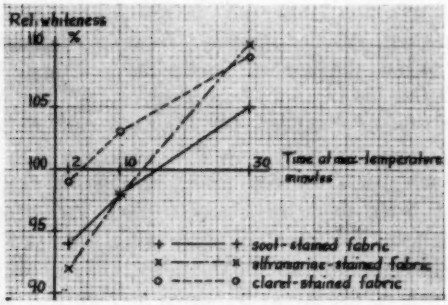


FIG. 4. *Influence of time at maximum temperature on the detergent action.*

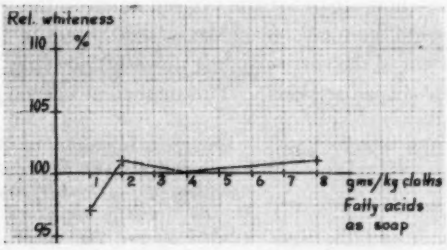


FIG. 5. *Influence of soap concentration on the average detergent action on soot-, ultramarine-, and claret-stained fabrics.*

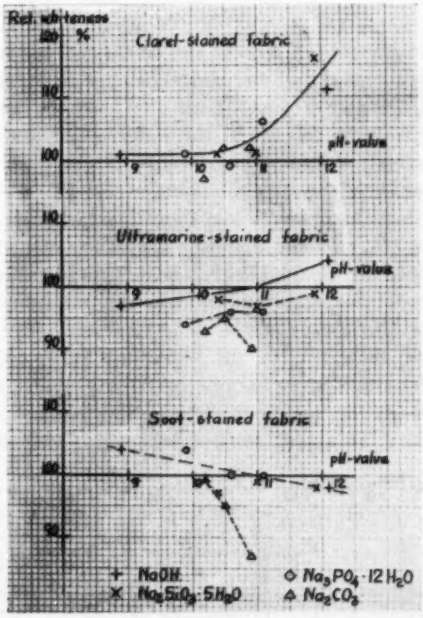


FIG. 6. *Influence of alkali concentration (pH value) on the detergent action.*

the alkali concentration cannot be recommended as a general method of increasing the detergent effect on all types of impurities.

At low alkali concentrations there seems to be little difference between the different alkalies as regards their average detergent effect in combination with soap. At the higher alkali concentrations used in these tests soda ash shows a poorer detergent effect than the other alkalies, of which sodium hydroxide and metasilicate seem to be the most effective, particularly the hydroxide. However, the test results are not sufficiently comprehensive to warrant a definite classification of the alkalies in this respect, at different maximum temperatures. The results obtained by Morgan [2] also indicate the above relationship between the various alkalies. Morgan likewise explicitly pointed out that relatively high concentrations of sodium hydroxide impair the washing results as far as soot-stained fabrics are concerned.

Effect of Maximum Temperature, Time at Maximum Temperature, and Concentration of Washing Agents on the Strength, Weight, Ash Content, and Whiteness of Bleached Cotton and Linen Fabric Subjected to Repeated Washing

No washing of textiles can be carried out without some chemical and mechanical damage to the fabrics. This damage reduces both the strength and the weight of the fabric. If the water is not practically completely soft, the loss of weight is wholly or partly compensated by precipitations on the fabric of calcium and magnesium soaps and the carbonates, silicates, etc., of these metals. The ash content of the fabrics after the washes gives some idea of the amount of such precipitations. Should the ash content of the washed fabric be the same as or not appreciably higher than that of the unwashed fabric (0.1%–0.2%), such precipitations have been added to the fabric in the course of the washing process to no extent or to a very small extent. The whiteness of bleached fabric that has been washed repeatedly is generally affected by such precipitations. When a clean fabric is washed together with soiled clothes, its whiteness may also be reduced by the precipitation of dirt on the fabric. Such precipitation may occur in connection with the precipitation of water hardeners. The dirt dispersed in the wash liquor may be precipitated on the fabric even in absolutely soft water, especially if the amount of soap used is inadequate. A strong dilution of the wash liquor by the use of a relatively large quantity of water for the first rinses is probably a contributory cause of these precipitations.

The changes in the strength, weight, ash content, and whiteness of the fabric are normally so slight as not to be noticeable after a single wash. A large number of washes are required for that purpose. One-hundred washes were carried out for the purpose of the investigations described here, and the strength, weight, ash content, and whiteness of the washed cotton and linen fabrics were determined after 50 and 100 washes. In some cases the weight was determined after 10 and 25 washes as well. The tensile strength of the fabric was used as a measure of strength.

The cotton fabric used in this investigation was two-shaft, bleached sheeting. Its weight was 210 g./sq. m., and the number of warp and weft threads was 250 and 234 per dm., respectively. The linen fabric consisted of bleached, two-shaft sheeting weighing 210 g./sq. m. and with 245 warp and 238 weft threads per dm. Six pieces of each fabric, each piece being about the size of a towel, were used for each test. Of these six, three were tested after 50 washes and three after 100 washes. The pieces were cut out of the fabric as shown in Figure 7, which illustrates the selection of test pieces for four series, *A*, *B*, *C*, and *D*, to be washed 50 and 100 times, and shows how strips for the determination of the tensile strength were cut out of the washed pieces of fabric and out of the corresponding unwashed sheeting (the cross-shaped sections). This method of selecting test

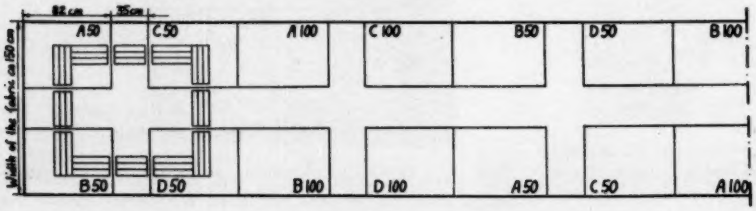


FIG. 7. *Sampling of fabric pieces and test strips for determination of the tensile strength of the fabric, unwashed and washed 50 and 100 times. For each wash method, three pieces were cut out for 50 washes and three for 100 washes.*

pieces was described in detail by the writer in *Melliand Textilberichte* **20**, 1939, p. 748.

For the determination of the tensile strength, the strips taken from the washed pieces of fabric were selected so as to have been in a line with the strips taken from the corresponding unwashed sheeting (as shown in Figure 7). The width of the unwashed strips was 50 mm., and the corresponding washed strips were made to contain the same number of longitudinal threads as the unwashed strips. Since three warp and three weft strips were taken from each piece of fabric, the tensile strength values obtained are the mean values of nine determinations in each direction. The tensile strength was in all cases determined on air-dry test strips at 65% R.H. with a Schopper strength tester for fabrics, with 200 mm. free length clamped between the jaws of the machine.

Between washes the pieces of fabric were centrifuged and dried by mangling (cylinder calender, steam-pressure 6–7 atm.), except in one case where the fabric was dried for 30 min. in air at about 50°C.

Reduction of the Tensile Strength of Cotton and Linen Fabric

Effect of the maximum temperature.—The effect of different maximum washing temperatures, other variables being equal, is shown in Table XII. The maximum temperature was varied between 65°C and 95°C. The series washes were carried out with soap and 1 g. and 4 g., respectively, of NaOH and 3 g. of Na_2CO_3 per kg. of clothes. The time at maximum temperature was 10 min. and the total washing time 30 min., except in the case of one series, in which the time at maximum temperature was 30 min. and the total washing time 50 min.

The reduction of the tensile strength of cotton fabric caused by 100 washes does not appear to have been appreciably affected by an increase of the maximum temperature from 65°C to 95°C when the time at maximum temperature was 10 min. When the latter time was 30 min., however, an increase of the temperature from 80°C to 95°C resulted in decidedly

TABLE XII. EFFECT OF THE MAXIMUM TEMPERATURE; THE REDUCTION OF TENSILE STRENGTH (%) OF COTTON AND LINEN FABRIC CAUSED BY 50 AND 100 WASHES *

Kind and amount of alkali per kg. wash goods →	1 g. NaOH						4 g. NaOH						4 g. NaOH						3 g. Na_2CO_3					
Time at max. temperature →	10 min.						10 min.						30 min.						10 min.					
	Warp		Weft		Average		Warp		Weft		Average		Warp		Weft		Average		Warp		Weft		Average	
No. of washes →	50	100	50	100	50	100	50	100	50	100	50	100	50	100	50	100	50	100	50	100	50	100	50	100
Max. temp. (°C)																								
Cotton fabric																								
65	11	16	12	15	12	15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
80	11	11	14	20	13	15	11	15	10	14	10	15	14	14	14	18	14	16	12	13	14	15	13	14
95 (90) (90)	14	17	12	14	13	15	15	13	10	13	12	13	11	21	14	21	13	21	14	15	10	13	12	14
Linen fabric																								
65	23	28	22	23	23	26	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
80	21	31	16	16	18	23	23	26	19	19	21	22	20	27	21	26	21	26	26	25	18	19	22	22
95 (90) (90)	19	25	16	24	17	24	20	28	13	28	17	28	23	31	21	33	22	32	17	26	22	17	19	21

Averages for the series

	Cotton fabric				Linen fabric			
Time at max. temp. →	10 min.		30 min.		10 min.		30 min.	
No. of washes →	50	100	50	100	50	100	50	100
Max. temp. (°C)								
65	12	16	—	—	23	26	—	—
80	12	15	14	16	20	22	21	26
95 (90)	12	14	13	21	18	24	22	32

* For every washing was used a quantity of soap corresponding to 4 g. fatty acid per kg. wash goods.

greater reduction of the tensile strength after 100 washes.

Analysis of variance of the values in Table XII for cotton fabric after 100 washes gives $F = 2.84$, which is highly significant since the value for the 1% limit is 2.65. If the *t*-test is applied, it appears that a difference between two means for significance at the 5% limit should be 3.48. Only the mean value for 100 washes with 4 g. NaOH for 30 min. at 95°C is thus significantly higher than the others. This is confirmed by the fact that an analysis of variance of all other values gives $F = 1.76$ at 7 and 136 degrees of freedom, which proves that there is no statistically significant difference between those values.

Analysis of variance of the values in Table XII for linen fabric gives $F = 3.33$, which indicates significant differences between the averages. The *t*-test proves that the value (32) after 100 washes with 4 g. NaOH for 30 min. at 95°C deviates significantly from all other values, except for that obtained when washing at the same temperature for 10 min. An analysis of variance of all values except that obtained when washing 100 times with 4 g. NaOH for 30 min. at 95°C gives an F value of 1.18, which is not significant. The statistical analysis consequently shows that when washing cotton and linen fabric, an increase of the temperature from 65°C to 95°C does not increase the damage to the fabric enough to cause a significantly greater reduction of their tensile strengths after 100 washes, provided the time at maximum temperature is 10 min. On the other hand, if the time at maximum temperature is prolonged to 30 min., a temperature increase from 80°C to 95°C results in a significantly greater reduction of the tensile strength of both types of fabrics. This does not, however, necessarily mean that an increase of the temperature from 65°C to 95°C is without any effect on the fabrics even if the time at these temperatures is 10 min. only. The results show only that the spread of the values for the reduction of the tensile strength is so great that any effect of the temperature increase might be disguised. Had each series comprised a considerably greater number of washes—*e.g.*, 200 or 300—it is possible that the effect of the temperature would have been evident in a reduction of tensile strength. That the use of higher temperatures really causes greater damage to fabric is proved by the loss of weight (see pp. 192–3).

It may be concluded that in practice the temperature can be raised up to 95°C without risking any appreciable increase of the damage to white cotton and linen clothes, provided that the time at maximum temperature does not exceed 10 min. and the total washing time 30 min. This applies to articles which are not subjected to more than about 100 washes. However, temperatures higher than those required to make the clothes adequately clean should obviously not be used unless special conditions make it absolutely necessary.

Effect of time at maximum temperature.—The effect of the time at maximum temperature has been studied by means of a series of washing tests with soap and 1 g. and 4 g., respectively, of NaOH, 4 g. of $Na_3PO_4 \cdot 12H_2O$, and 9 g. of Na_2CO_3 per kg. wash goods. In all these tests the soap concentration corresponded to 4 g. of fatty acid per kg. of clothes. The time at maximum temperature was 10 min. and 30 min. (one series 20 min.), which means a total washing time of 30 min. and 50 min. (one series 40 min.), respectively. The series (with 1 g. NaOH) where the time at maximum temperature was 20 min. has in the following discussion been included with the 30-min. series. The maximum temperatures were 80°C and 95°C. The results are shown in Table XIII.

Analysis of variance of the values in Table XIII after 100 washes of cotton fabrics at maximum temperature 80°C gives $F = 3.45$, which roughly corresponds to an 8% probability that the difference found between the values for 10 min. and 30 min. at maximum temperature would appear even if there was no actual difference. Such a difference is usually not considered significant. Cotton fabric after 100 washes at maximum temperature 95°C gives $F = 7.94$, which is highly significant. It does not fall within the 1% limits.

The same computation for linen fabric washed 100 times at maximum temperature 80°C gives $F = 2.33$, and at maximum temperature 95°C gives $F = 14.97$. The former value indicates no but the later value a high significance.

The test results indicate that an increase of the washing time from 10 to 30 min. has in practice little or no effect on the strength reduction of cotton and linen fabric, provided the maximum temperature is not too high—*i.e.*, not more than about 80°C. However, the effect of the time factor on the tensile strength is increased with increasing temperature, so that 100 washes for 30 min. at 95°C (total washing time 50 min.) causes a significantly greater loss of tensile strength than 100 washes for 10 min. at that temperature (total washing time 30 min.).

TABLE XIII. EFFECT OF TIME AT MAXIMUM TEMPERATURE; TENSILE STRENGTH REDUCTION (%) AFTER 50 AND 100 WASHES *

Kind and amount of alkali per kg. clothes	Max. temp. (°C)	Time at max. temp. (min.)	Cotton fabric Warp 50	Cotton fabric Warp 100	Cotton fabric Weft 50	Cotton fabric Weft 100	Cotton fabric Average 50	Cotton fabric Average 100	Linen fabric Warp 50	Linen fabric Warp 100	Linen fabric Weft 50	Linen fabric Weft 100	Linen fabric Average 50	Linen fabric Average 100
1 g. NaOH	80	10	11	11	14	20	13	15	21	31	16	16	18	23
	80	20	6	16	9	17	8	17	22	31	12	18	17	24
4 g. NaOH	80	10	11	15	10	14	10	15	23	26	19	19	21	22
	80	30	14	14	14	18	14	16	20	27	21	26	21	26
4 g. NaOH	95	10	15	13	10	13	12	13	20	28	13	28	17	28
	95	30	11	21	14	21	13	21	23	31	21	33	22	32
4 g. $Na_3PO_4 \cdot 12H_2O$	80	10	11	14	12	11	12	12	21	31	18	29	19	30
	80	30	12	15	9	16	11	16	19	36	18	30	19	33
9 g. Na_2CO_3	95	10	9	14	13	18	11	16	15	22	12	21	13	21
	95	30	15	19	12	25	14	22	20	35	13	26	17	31

Averages for the series

No. of washes →	80°C 50	80°C 100	95°C 50	95°C 100
Cotton fabric				
10 min.	12	14	12	15
20–30 min.	11	16	14	22
Linen fabric				
10 min.	21	25	15	25
20–30 min.	19	28	20	32

* High-titer soap at a concentration corresponding to 4 g. fatty acid per kg. wash goods was used for all these tests.

TABLE XIV. EFFECT OF ALKALI CONCENTRATION AND KIND OF ALKALI USED; TENSILE STRENGTH REDUCTION (%) AFTER 50 AND 100 WASHES *

Kind and amount of alkali per kg. wash goods	Max. temp. (°C)	Time at max. temp. (min.)	pH value of the liquor	Cotton fabric Warp 50	Cotton fabric Warp 100	Cotton fabric Weft 50	Cotton fabric Weft 100	Cotton fabric Average 50	Cotton fabric Average 100	Linen fabric Warp 50	Linen fabric Warp 100	Linen fabric Weft 50	Linen fabric Weft 100	Linen fabric Average 50	Linen fabric Average 100
0.5 g. NaOH	80	10	8.9	8	12	11	12	9	12	25	29	16	24	20	26
1.0 g. NaOH	80	10	11.0	11	11	14	20	13	15	21	31	16	16	18	23
4.0 g. NaOH	80	10	12.1	11	15	10	14	10	15	23	26	19	19	21	22
1.0 g. NaOH	95	30	11.0	12	15	12	17	12	16	21	34	12	26	16	30
4.0 g. NaOH	95	30	12.1	11	21	14	21	13	21	23	31	21	33	22	32
2.0 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	9.8	15	13	13	17	14	15	22	36	19	24	20	30
5.0 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	11.0	13	15	11	17	12	16	21	24	18	27	19	26
10.0 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	11.8	7	18	8	17	7	18	20	30	16	28	18	29
3.0 g. Na_2CO_3	95	10	10.2	14	15	10	13	12	14	17	26	22	17	19	21
9.0 g. Na_2CO_3	95	10	10.5	9	14	13	18	11	16	15	22	12	21	13	21
5.0 g. $Na_3H(CO_3)_2 \cdot 2H_2O$	80	10	9.8	11	13	10	13	11	13	19	27	12	21	15	24

* High-titer soap corresponding to 4 g. fatty acid per kg. wash goods was used for all these washing tests.

Effect of alkali concentration.—For the purpose of this investigation, washing series were carried out: in accordance with time-temperature schedule *1* (Figure 1), maximum temperature 80°C for 10 min. with 0.5, 1.0, and 4.0 g. NaOH and 2.0, 5.0, and 10.0 g. $Na_2SiO_3 \cdot 5H_2O$ and 5.0 g. $Na_3H(CO_3)_2 \cdot 2H_2O$; in accordance with time-temperature schedule *4* (Figure 1), maximum temperature 95°C for 30 min. with 1.0 and 4.0 g. NaOH; and in accordance with time-temperature schedule *3* (Figure 1), maximum temperature 95°C for 30 min. with 3.0 g. and 9.0 g. Na_2CO_3 per kg. wash goods. Soap corresponding to 4.0 g. fatty acid per kg. clothes was used for all the tests.

The results (Table XIV) show that when the time at maximum temperature is 10 min., the variations of the alkali concentration within the limits stated above do not appear to have any appreciable effect on the reduction of the tensile strength after 100 washes. That a high alkali concentration may cause a relatively great reduction of the tensile strength if the maximum temperature is high and the time at that temperature is long is proved by the results of washes with NaOH at 95°C for 30 min.

The average pH values of the wash liquors are shown in the table. The determinations were made on liquor drawn off from the washing machine after the washing. The pH values were determined by means of a hydrogen electrode at 20°C. The pH value varied between 8.9 and 12.1 for the different concentrations and kinds of alkali used.

Of the different kinds of alkali, metasilicate shows a tendency to cause greater damage to the fabrics than sodium hydroxide, for example. This applies particularly to linen fabric. An analysis of variance of the values for tensile strength reduction after 100 washes with the three different concentrations of sodium hydroxide and metasilicate at 80°C (for 10 min.) gives F values of 4.01 for cotton fabric and 8.43 for linen fabric at 1 and 106 degrees of freedom, respectively. The F value for the cotton fabric closely corresponds to the 5% limit, which makes it difficult to say whether the difference is significant. The F value for the linen fabric, on the other hand, is above the 1% limit, and must therefore be deemed to indicate a significantly greater reduction of the tensile strength of this fabric when washed with metasilicate than when washed with sodium hydroxide, at least when the metasilicate amounts to 10 g. per kg. wash goods. This is due, no doubt, to the fact that when metasilicate is used the fibers absorb a certain amount of silica from the wash liquor, even in practically soft water. The amount of silica absorbed by the cotton fiber is, however, very small and without any practical importance. The linen fiber, on the other hand, absorbs a much greater amount (see Table XVI, which shows the ash contents of the washed fabrics).

Effect of high- and low-titer soaps.—Washing series in which different kinds of soaps were used show, within the limits of accuracy, the same reduction of tensile strength after 100 washes in all cases in which the iodine values of the fatty acids were relatively low (35–60). Two washing series were carried out with soap made of fatty acids with a relatively high iodine value (115) (see Table XV). In one of the series the pieces of fabric were dried quickly by mangling between each wash, and in the other one they were dried more slowly in a dryer at about 50°C. The reduction of the tensile strength

TABLE XV. EFFECT OF HIGH- AND LOW-TITER SOAPS; TENSILE STRENGTH REDUCTION (%) AFTER 50 AND 100 WASHES *

			Cotton fabric						Linen fabric					
			Warp		Weft		Average		Warp		Weft		Average	
No. of washes →			50	100	50	100	50	100	50	100	50	100	50	100
Titer (°C)	Acid value of fatty acids	Iodine value												
40	200	60	11	11	14	20	13	15	21	31	16	16	18	23
17	231	35	11	11	12	12	11	12	20	24	18	26	19	25
20	166	115†	9	13	9	11	9	12	23	32	20	33	21	33
		‡	13	18	11	18	12	18	36	43	25	42	30	42

* A soap concentration corresponding to 4 g. fatty acid plus 1 g. NaOH per kg. wash goods was used for all washing tests. The maximum temperature was 80°C for 10 min. (time-temperature schedule is shown in Figure 1).

† The pieces of fabric were dried by mangling between each wash. Drying time, about 1 min.

‡ The pieces of fabric were dried between each wash in a dryer at about 50°C. Drying time, about 30 min.

of the cotton fabric caused by 100 washes with this soap combined with quick drying was the same as that caused by using the other soaps. Slow drying, on the other hand, tended to increase the reduction of the tensile strength. The effect of the soap with the high iodine value was more marked on the linen fabric, as was also the difference between quick and slow drying. This confirms an earlier observation made at The Government Testing Institute [3]—*viz.*, that washing with soaps of highly unsaturated fatty acids results, or may result, in a relatively great reduction of the tensile strength of cotton and linen fabric. This seems to be connected with oxidation of the unsaturated fatty acids from the soap which may remain on the fabric. It would seem that this oxidation occurs mainly during the drying process, peroxides being formed. The slower the drying, the greater the effect of this oxidation.

Change of Weight and Ash Content of Cotton and Linen Fabric

When a fabric is washed, it loses some of its fiber material. This loss is partly due to the fact that fibers are mechanically detached from the fabric and removed with the wash liquor. This is known by every laundryman. In addition, a small amount of fiber substance is dissolved in the alkaline liquor. It is, no doubt, primarily degenerated cellulose—*e.g.*, oxycellulose—that is dissolved. Quantitatively, the total loss of fiber can be determined by weighing the pieces of fabric before and after washing. The difference in weight indicates the loss of fiber, provided that no foreign matter has been added to the fabric in the course of the washing—*e.g.*, in the form of calcium soaps—which wholly or partly compensates the loss of fiber. If the loss of weight is to be a measure of the loss of fiber, all dressing must be removed from the fabric before it is washed and weighed.

In all of the washing series included in the I.T. investigations the loss of weight was determined after 50 and 100 washes, and in some series after 10 and 25 washes as well.

The loss of weight was determined by weighing the pieces of fabric, air-dried at 65% R.H., before and after the washes. The loss of weight for each kind of fabric after 100 washes is given as the average of three separate determinations, one for each of the three pieces of fabric washed, and is given as a percentage of the weight before washing.

As may be seen from Figure 8, the weight reduction is greatest during the first 25 washes and is then smaller and roughly proportional to the number of washes. Whether or not the relatively large weight reduction during the first washes is due to a greater amount of loose fibers being detached has not been determined, but seems quite likely. It is, however, also possible that there is a relatively large amount of soluble matter in the fibers of the unwashed, bleached fabric which may contribute to the relatively large weight reduction in the first washes. That some of the fiber material is really dissolved is proved by the fact that an increase of the alkalinity of the wash liquor, other conditions being equal, results in increased weight reduction. It is hardly possible that variations in alkalinity (within the limits fixed for this investigation) should have any effect on the mechanical loss of fiber.

Figures 9 and 10 show the relation between the loss of weight and the reduction of tensile strength. On the graph for cotton fabric (Figure 9) the points are reasonably well located along one line; for the linen fabric (Figure 10) they are more widely spread. This is at least partly due to the relatively great margin of error in the averages of the tensile strength reduction, which is much greater for linen than for cotton fabric. There seem to be other factors also, at least with regard to linen fabric—*e.g.*, the loss of weight is relatively small but the tensile strength reduction is large for fabric washed with soaps of highly unsaturated fatty acids. Whether or not this anomaly is due to some special influence on the fiber material of the fabric will perhaps be revealed by the investigation of the viscosity of fiber material solutions which is now in progress.

TABLE XVI. ASH CONTENTS (%) OF FABRICS WASHED WITH DIFFERENT CONCENTRATIONS OF METASILICATE *

	Bleached cotton fabric		Bleached linen fabric	
No. of washes ⟶	50	100	50	100
Amount of $Na_2SiO_3 \cdot 5H_2O$ per kg. wash goods				
2 g.	0.09	0.07	0.49	0.53
5 g.	0.09	0.09	0.67	1.34
10 g.	0.12	0.25	1.26	2.93

* Ash content of unwashed cotton fabric, 0.07%; of linen fabric, 0.27%.

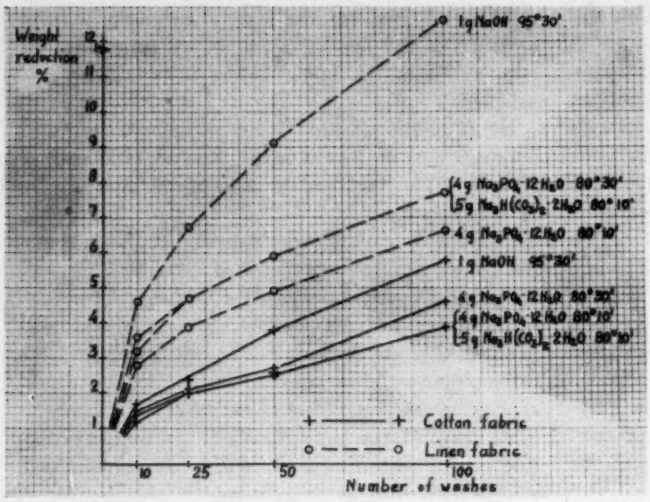


FIG. 8. *Relation between weight reduction and number of washes for cotton and linen fabrics.*

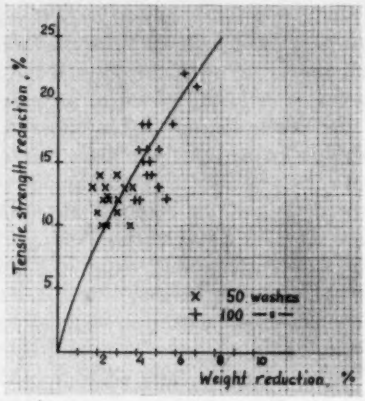


FIG. 9. *Relation between weight reduction and tensile strength reduction after 50 and 100 washes for cotton fabric.*

Tables XVII, XVIII, and XIX show the weight reduction of cotton and linen fabric after 50 and 100 washes. Figures 11, 12, and 13 show these data graphically. There are only two points plotted for each variable; to make the graphs clear, these points are connected by straight lines. However, this does not mean that the weight reduction in each case is directly proportional to the variable.

Figure 11 shows that an increase of the maximum temperature from 80°C to 95°C increases the percentage weight reduction in cotton fabric by 0.2–0.6 unit only after 100 washes when the time at maximum temperature is 10 min. If the time at maximum temperature is 30 min., the difference in the weight reduction between 80°C and 95°C is greater—*viz.*, nearly 2 units. Linen fabric is affected to a far greater extent by an increase of temperature. At 80°C the weight reduction of linen fabric is about 1.5 times as great and at 95°C about twice as great as that of cotton fabric.

Figures 11 and 12 show that a prolongation of the time at maximum temperature (80°C) from 10 to 30 min. has about the same effect on the weight reduction as an increase of the temperature from 80°C to 95°C when the time is 10 min. It can also be found that a prolongation of the time at 95°C from 10 to 30 min. has about the same effect on weight reduction as an increase of the temperature from 80°C to 95°C when the time at maximum temperature is 30 min.

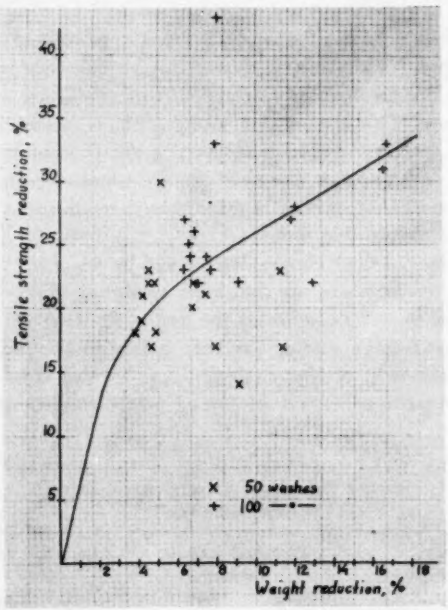


FIG. 10. *Relation between weight reduction and tensile strength reduction after 50 and 100 washes for linen fabric.*

The effect of the alkali concentration on the weight reduction is shown in Figure 13. As may be seen from the graph, an increase of the alkali concentration —within the limits fixed for these tests—causes only a small increase of the weight reduction of cotton

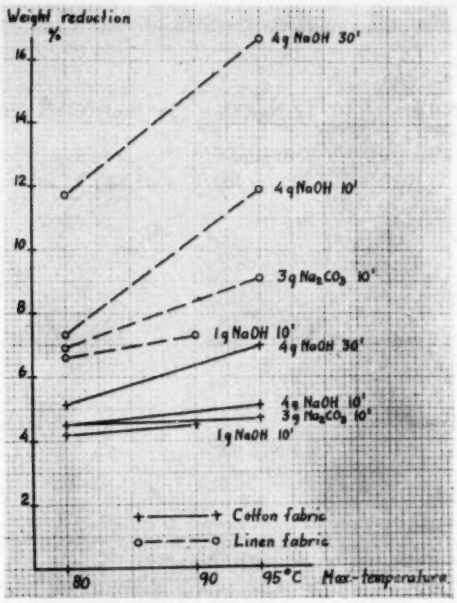


FIG. 11. *Influence of maximum temperature on the weight reduction of the fabrics after 100 washes.*

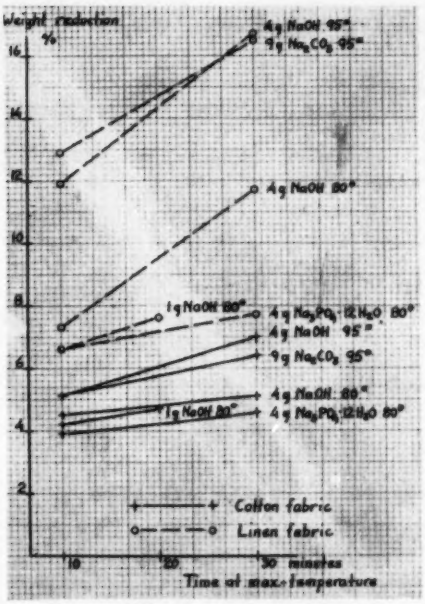


FIG. 12. *Influence of time at maximum temperature on the weight reduction of the fabrics after 100 washes.*

fabric when the time at maximum temperature is 10 min. This is also the case for a time of 30 min. at a maximum temperature of 80°C. If the maximum temperature is increased to 95°C and the time to 30 min., the alkali concentration has a considerably greater effect on the weight reduction. The weight reduction of linen fabric is not appreciably affected by an increased alkali concentration so long as the maximum temperature does not exceed 80°C and the time at that temperature is 10 min. This may also be seen from Figure 11, where the lines for the 10-min. period converge towards the temperature of 80°C. If the temperature is increased to 95°C, the linen fabric is affected to a much greater extent than the cotton fabric, especially if the time at maximum temperature is prolonged to 30 min.

Because of the relatively great effect on linen fabric of an increase of the time and the temperature, it is of great importance that this kind of fabric be washed at a maximum temperature not exceeding 80°C and that the time at that temperature should not exceed 10 min. (total washing time, 30 min.). Should it be necessary to use higher temperatures or a longer time at maximum temperature in order to obtain satisfactory whiteness, the alkalinity of the wash liquor should be kept low.

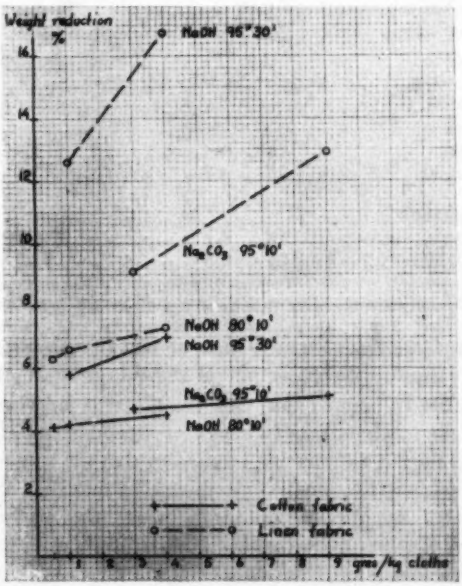


FIG. 13. *Influence of alkali concentration on the weight reduction of the fabrics after 100 washes.*

The investigation proves that the weight reduction of cotton and linen fabric after a large number of washes is a far more sensitive gage of the variants

TABLE XVII. EFFECT OF THE MAXIMUM TEMPERATURE ON WEIGHT REDUCTION (%) AFTER 50 AND 100 WASHES *

Kind and amount of alkali per kg. wash goods →	1 g. NaOH		4 g. NaOH		4 g. NaOH		3 g. Na_2CO_3		5 g. $Na_3H(CO_3)_2 \cdot 2H_2O$	
Time at max. temperature →	10 min.		10 min.		30 min.		10 min.		10 min.	
No. of washes →	50	100	50	100	50	100	50	100	50	100
Max. temp. (°C)										
Cotton fabric										
65	2.4	4.1	—	—	—	—	—	—	—	—
80	1.6	4.2	2.2	4.5	2.1	5.1	2.4	4.5	2.5	3.9
95 (90) (90)	2.3	4.5	2.9	5.1	3.7	7.0	3.0	4.7	—	—
Linen fabric										
65	4.5	6.8	—	—	—	—	—	—	—	—
80	3.8	6.6	4.3	7.3	7.3	11.7	4.7	6.9	5.9	7.7
95 (90) (90)	4.8	7.3	7.9	11.9	11.2	16.7	6.7	9.1	—	—

* Soap corresponding to 4 g. fatty acid per kg. wash goods was used.

TABLE XVIII. EFFECT OF THE TIME AT MAXIMUM TEMPERATURE ON WEIGHT REDUCTION (%) CAUSED BY 50 AND 100 WASHES *

Kind and amount of alkali per kg. wash goods →	1 g. NaOH		4 g. NaOH		4 g. NaOH		$Na_3PO_4 \cdot 12H_2O$		9 g. Na_2CO_3	
Max. temperature →	80		80		95		80		95	
No. of washes →	50	100	50	100	50	100	50	100	50	100
Time at max. temp. (min.)										
Cotton fabric										
10	1.6	4.2	2.2	4.5	2.9	5.1	2.6	3.9	3.0	5.1
(20) 30 (20)	2.1	4.7	2.1	5.1	3.7	7.0	2.7	4.6	3.4	6.4
Linen fabric										
10	3.8	6.6	4.3	7.3	7.9	11.9	4.9	6.6	9.1	12.9
(20) 30 (20)	4.6	7.6	7.3	11.7	11.2	16.7	5.8	7.7	11.3	16.5

* Soap corresponding to 4 g. fatty acid per kg. wash goods was used.

studies—*i.e.*, temperature, time, and alkali concentration—than is the reduction of the tensile strength. As already pointed out, this is only true provided that no precipitations to speak of are added to the fabric during the washing process, or that the amount of such precipitations is determined, or that they are removed by special treatment before the washed pieces of fabric are weighed. The ash content of the fabrics has been used as a means of determining whether any appreciable amount of precipitation has been added during the washing process. The ash content of the cotton fabric varied between 0.03% and 0.18% after 100 washes (before the washing, 0.06%–0.07%), and that of the linen fabric between 0.13% and 0.22% for fabric having 0.16% ash when unwashed, and 0.32%–0.62% for fabric having 0.23%–0.28% ash when unwashed. The fabrics washed with soap and metasilicate, the ash contents of which are shown in Table XVI, are not included in the above discussion.

Whiteness of Cotton and Linen Fabric after 50 and 100 Washes

After having been washed 50 and 100 times, the pieces of cotton and linen fabric were tested for degree of whiteness (total light reflection). The degree of whiteness is affected by the amount of colored particles of dirt reprecipitated into the fabric

TABLE XIX. EFFECT OF ALKALI CONCENTRATION AND KIND OF ALKALI ON WEIGHT REDUCTION (%) AFTER 50 AND 100 WASHES *

Alkali	Max. temp. (°C)	Time at max. temp. (min.)	Conc. (g.) per kg. wash goods	pH value of the liquor	Cotton fabric 50 washes	Cotton fabric 100 washes	Linen fabric 50 washes	Linen fabric 100 washes
NaOH	80	10	0.5	8.9	2.4	4.1	4.2	6.3
	80	10	1.0	11.0	1.6	4.2	3.8	6.6
	80	10	4.0	12.1	2.2	4.5	4.3	7.3
NaOH	95	30	1.0	11.0	3.8	5.8	9.1	12.6
	95	30	4.0	12.1	3.7	7.0	11.2	16.7
$Na_2SiO_3 \cdot 5H_2O$	80	30	2.0	9.8	2.9	4.3	4.7	5.7
	80	30	5.0	11.0	2.3	4.1	4.1†	4.7†
	80	30	10.0	11.8	2.3	4.2	3.6†	2.8†
Na_2CO_3	95	10	3.0	10.2	3.0	4.7	6.7	9.1
	95	10	9.0	10.5	3.0	5.1	9.1	12.9
$Na_3H(CO_3)_2 \cdot 2H_2O$	80	10	5.0	9.8	2.5	3.9	5.9	7.7

* High-titer soap of a concentration corresponding to 4 g. fatty acid per kg. wash goods was used in all washing tests.
† The relatively low values are due to increase in the ash content of the fabrics.

during the washing. The amount of reprecipitated impurities depends on the nature of the water and the dirt content of the clothes washed with the test fabrics. If the water is hard, calcium and magnesium compounds, usually in the form of soap, are precipitated into the wash goods, especially during rinsing, when dirt remaining in the water is also partly or wholly precipitated on the clothes. If the water contains iron or manganese, the color of the soaps is affected to some extent and the clothes may take on a greyish yellow or yellowish grey color. Should the calcium and magnesium soaps precipitated on the fabric contain any appreciable quantity of unsaturated fatty acids, which turn yellow when oxidized, this may contribute to yellowing. Only softened water with a hardness of less than 1°dH was used for the present investigations. The amount of precipitations of calcium and magnesium compounds was therefore insignificant, and had little or no effect on the whiteness of the fabrics. The dirt content of the clothes washed with the test fabrics, on the other hand, may have varied, even though it was, on the whole, practically uniform. It is possible that the last wash or washes before measuring affected the degree of whiteness to some extent. Therefore, one should not pay too much attention to slight variations in the relative whiteness. The results are shown in Table XXI. All of the measurements were made after all of the washes had been completed.

TABLE XX. EFFECT OF HIGH- AND LOW-TITER SOAPS; WEIGHT REDUCTION (%) AFTER 50 AND 100 WASHES *

Fatty acids: Titer (°C)	Fatty acids: Acid value	Fatty acids: Iodine value	Cotton fabric 50 washes	Cotton fabric 100 washes	Linen fabric 50 washes	Linen fabric 100 washes
40	200	60	1.6	4.2	3.8	6.6
17	231	35	2.0	3.9	4.1	6.5
20	166	115†	3.6	5.4	4.6	7.9
		‡	2.9	5.8	5.1	8.0

* Soap corresponding to 4 g. fatty acid and 1 g. NaOH per kg. wash goods was used for all washing tests. Maximum temperature, 80°C for 10 min.
† The pieces of fabric were dried by mangling between washes. Drying time, about 1 min.
‡ The pieces of fabric were dried between washes in a dryer at about 50°C. Drying time, about 30 min.

After being boiled in water, the unwashed cotton fabric showed a whiteness of 87%–89%; the unwashed linen fabric used for the washing tests with 0.5 and 1.0 g. NaOH (except at 95°C for 30 min.), with 4 g. NaOH at 80°C for 10 min., and with metasilicate showed a whiteness of 77%, and that used for all of the other washing tests 68%–70%.

The original degree of whiteness of the linen fabric used for most of the tests was thus comparatively low, which means that it was not completely bleached according to conventional standards. The whiteness

of this kind of fabric was, therefore, as a rule increased by the washing.

The original degree of whiteness of the cotton fabric was high, and decreased by about 6 to 12 units after 50 washes. After another 50 washes—*i.e.*, 100 washes in all—the whiteness was further decreased by up to 3 units. When the fabric was washed with high-titer soap and 1 g. NaOH, the whiteness after 100 washes was found to be somewhat lower when the maximum temperature was higher. This was due, however, to discoloration from some garment that was washed with it at the same time. On the average, washing with high-titer soap and NaOH resulted in a somewhat higher degree of whiteness than washing with other alkalies. The comparatively low whiteness of cotton fabric washed with low-titer soap and NaOH is worthy of note. This may possibly be due to the poorer "dirt-carrying" properties of this kind of soap as compared with those of high-titer soap. The whiteness of the fabric washed with soap and metasilicate decreased when the amount of silicate was increased. This is probably connected with the fact that the ash content of the fabric was increased with the silicate concentration.

Summary

The object of this investigation was to determine the effects of the maximum temperature, the time, and the concentration of washing agents on the detergent action of the washing and on the reduction of the tensile strength and of the weight of bleached cotton and linen fabric.

TABLE XXI. THE RELATIVE DEGREE OF WHITENESS (% OF THE WHITENESS OF A PLATE COATED WITH MAGNESIUM OXIDE) OF COTTON AND LINEN FABRIC AFTER 50 AND 100 WASHES *

Kind and amount of alkali per kg. wash goods	Max. temp. (°C)	Time at max. temp. (min.)	No. of washes → Cotton fabric 50	Cotton fabric 100	Linen fabric 50	Linen fabric 100
High-titer soap						
0.5 g. NaOH	80	10	82	80	82	80
1 g. NaOH	65	10	82	80	82	82
	80	10	82	79	82	82
	80	20	81	78	81	80
	90	10	76	76	78	79
	95	30	82	81	77	78
4 g. NaOH	80	10	82	81	81	80
	80	30	80	79	74	74
	95	10	83	81	75	73
	95	30	83	82	76	77
4 g. $Na_3PO_4 \cdot 12H_2O$	80	10	80	77	75	76
	80	30	79	78	75	76
2 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	81	78	77	77
5 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	81	77	76	76
10 g. $Na_2SiO_3 \cdot 5H_2O$	80	10	80	76	76	74
3 g. Na_2CO_3	80	10	78	76	75	77
	95	10	80	77	77	76
9 g. Na_2CO_3	95	10	79	78	77	78
	95	30	79	78	78	78
5 g. $Na_3H(CO_3)_2 \cdot 2H_2O$	80	10	79	76	77	77
Low-titer soap						
1 g. NaOH						
Low iodine value	80	10	78	75	72	70
High iodine value	80	10†	78	75	69	66
High iodine value	80	10‡	79	76	72	70

* Soap corresponding to 4 g. fatty acid per kg. wash goods was used for all washing tests.
† Mangling dryer.
‡ Air dryer (50°C).

The increase in the whiteness of cotton fabric stained with soot, paraffin oil, and tallow, with ultramarine, and with claret after three washes was used as a measure of the detergent action. The increase in whiteness was also determined after one wash, and in some cases after two washes.

The reduction of the tensile strength and of the weight of cotton and linen fabric was determined after 50 and 100 washes, and in some cases after 10 and 25 washes as well. The ash content and the whiteness of the washed pieces of fabric were determined after 50 and 100 washes. The method used for cutting the requisite pieces of fabric and test strips may be seen from Figure 7.*

All washing tests were carried out in connection with the practical work in the laundry of a Stockholm hospital. Softened Stockholm water was used for all washing tests. The quantity of water added for each operation was measured by means of a water meter fitted into the intake pipe. A one-wash process, consisting of soaking, washing, and five rinses, was used for all tests. In each case 8.0 liters of water per kg. wash goods was added for the soaking, 1.5 liters for the washing, 1.5 liters for the first rinse, 3.0 liters for the second rinse, and 6.0 liters for each of the following three rinses. During or after the last rinse, 0.64 ml. glacial acetic acid per kg. wash goods was added for souring. The temperature-time schedules used are shown in Figure 1.

Soap made of fatty acids with a titer of about 40°C was used for the washing tests, except in special tests with low-titer soap made of fatty acids with low and high iodine values, respectively. Of the common alkalies, sodium hydroxide, sodium metasilicate, trisodium phosphate, sodium carbonate, and sodium sesquicarbonate were used.

A total of about 3,000 washing tests were carried out for the purpose of this investigation, the main results being as follows.

Detergent Effect

Increasing the maximum washing temperature within the interval of 65°C to 95°C resulted in a continuous increase of the detergent effect. Increasing the time at maximum temperature between 2 and 30 min. also resulted in improved detergent action. Provided the time at maximum temperature is 10 min. (total washing time, 30 min.), an increase of that temperature from 80°C to 95°C appears, on an average, to have about the same effect on detergency as a prolongation of the time at a maximum temperature of 80°C from 10 to 30 min. (total washing time, 50 min.). (See Figures 3 and 4.)

An increase of the soap concentration over and above that required for the dispersion of the dirt does not appreciably improve the detergent effect. A distinct lathering of the soap solution in the machine is usually an indication that the soap concentration is adequate.

A higher alkali concentration may result in a poorer or better detergency than a lower concentration depending on the types of dirt on the wash goods. Certain types of dirt—*e.g.*, soot—are more easily removed with a lower alkali concentration than with a higher one. Other impurities—*e.g.*, coloring organic matter (claret)—are more easily removed when the alkalinity of the wash liquor is high than when it is low. As a rule, about 1 g. NaOH, about 3 g. $Na_2SiO_3 \cdot 5H_2O$, about 4 g. $Na_3PO_4 \cdot 12H_2O$, or about 3 g. Na_2CO_3 per kg. wash goods is sufficient. However, it should be borne in mind that the amount of free and loosely combined carbon dioxide in the water affects the alkalinity of the lye. A high percentage of carbon dioxide may require the addition of a larger amount of alkali. The pH value can be used to check the alkalinity of the liquor. For ordinary white goods the pH value of the wash liquor should be between $10\frac{1}{2}$–11, measured at 20°C. When using a comparatively weak alkali—*e.g.*, soda ash—such large amounts are required in order to attain that pH value that the detergent action of the wash liquor on impurities of the soot type is relatively low. In such cases, weak alkalies are not very suitable.

Effect on the Tensile Strength and the Weight Reduction of Cotton and Linen Fabric

At a total washing time of 30 min., 10 min. of which was at maximum temperature, the tensile strength of cotton fabric was reduced by about 15% and that of linen fabric by about 25% after 100 washes, irrespective of the maximum temperature within the range 65°C and 95°C (see Table XII). When using the time schedule mentioned, the maximum temperature may thus be increased from 65°C to 95°C when washing cotton and linen fabric without causing any noticeably larger loss of tensile strength after 100 washes. However, this does not mean that the temperature increase does not damage

* See also Köhler, *Melliand Textilberichte* **20**, 1939, p. 748.

the fabrics, but only that this damage is not sufficiently great to make any significant difference in the tensile strength reduction. That the damage is actually greater when the temperature is increased is proved by the loss of weight (loss of fiber) of the fabrics. (See Table XVII and Figure 11.) The loss of weight is greater at a maximum temperature of 95°C than at 80°C. For cotton fabric this difference is fairly small, while it is greater for linen fabric, particularly when the alkalinity is high.

At a maximum temperature of 80°C a prolongation of the time at that temperature from 10 to 30 min. does not cause any significant change in the tensile strength reduction of cotton and linen fabric after 100 washes. If the maximum temperature is raised to 95°C, other conditions being equal, a prolongation of the time from 10 to 30 min. causes a significantly greater loss of tensile strength, at least when the alkali concentrations used are as high as, for example, 4 g. NaOH or 9 g. Na_2CO_3. The loss of weight after 100 washes gives a more detailed picture of the effect of the time factor than does the reduction of tensile strength (see Table XVIII and Figure 12). The test results show that when the time at maximum temperature is 10 min., an increase of the temperature from 80°C to 95°C has, on the whole, the same effect on the weight reduction as a prolongation of the said time from 10 to 30 min. when the maximum temperature is 80°C; and if the time at maximum temperature is 30 min., an increase of that temperature from 80°C to 95°C has the same effect as a prolongation of the time at 95°C from 10 to 30 min. The heating time (up to maximum temperature) was assumed to be the same in all cases (20 min.). The variation of the alkali concentration within the limits fixed for these tests—0.5–4.0 g. NaOH, 2.0–10.0 g. $Na_2SiO_3 \cdot 5H_2O$, and 3.0–9.0 g. Na_2CO_3—does not seem to have any appreciable effect on the tensile strength reduction of cotton and linen fabric after 100 washes if the time at maximum temperature is 10 min. (total washing time, 30 min.) (see Table XIV). That a high alkali concentration may cause a relatively great loss of tensile strength if the maximum temperature is high and the time at that temperature is long is proved by the results of the washing tests with 4 g. NaOH at 95°C for 30 min. The tests show that the ash content of linen fabric in particular is increased when the fabric is washed with metasilicate, even if the water is practically soft. When a large amount of metasilicate is used, that increase is considerable. After 100 washes with 10 g. $Na_2SiO_3 \cdot 5H_2O$ per kg. wash goods, the ash content of the linen fabric amounted to nearly 3%. The loss of weight gives a more detailed picture of the effect of the alkali concentration on cotton and linen fabric than does the reduction of tensile strength (see Table XIX and Figure 13).

The washing tests with low-titer soaps made of fatty acids with low and high iodine values, respectively, have confirmed the observation made by The Government Testing Institute—*viz.*, that soap made of fatty acids with a high iodine value does more damage to cotton and particularly to linen than does soap made of fatty acids with a low iodine value. This damage is especially pronounced when the fabric is allowed to dry slowly, which fact may be due to the formation of peroxides in connection with the oxidation of fatty acids remaining on the fabric (see Table XV).

Literature Cited

1. Madsen, T., "Studies in the Detergent Action and Surface Activity of Soap Solutions," Copenhagen, Teknologisk Institut, 1931.
2. Morgan, O. M., *Can. J. Research* **6**, p. 292 (1932); **8**, pp. 429, 583–91 (1933).
3. Norlin, E., and Skärblom, K. J., *Statens Provningsanstalts, Stockholm, Medd.* No. 49 (1930).
4. Rhodes, F. H., and Bascom, C. H., *Ind. Eng. Chem.* **23**, 778 (1931).
5. Rhodes, F. H., and Brainard, S. W., *Ind. Eng. Chem.* **21**, 60 (1929).
6. Rhodes, F. H., and Wynn, C. S., *Ind. Eng. Chem.* **29**, 56 (1937).
7. Schnyder, A., "Untersuchungen über die Einflüsse von Wasch- und Bleichprozessen auf Baumwoll- und Leinengewebe," Ph.D. thesis, Biel, Switzerland, 1941.
8. Utermohlen, W. P., and Ryan, M. E., *Ind. Eng. Chem.* **41**, 2881 (1949).
9. Vaughn, T., and Vittone, A., Jr., *Ind. Eng. Chem.* **33**, 1011 (1941); **35**, 1094 (1943).

(Manuscript received May 8, 1953.)

TEXTILE RESEARCH INSTITUTE

LABORATORIES AND GENERAL OFFICES

PRINCETON, N. J.

PUBLICATIONS DEPARTMENT

10 EAST 40TH STREET, NEW YORK 16, N. Y.

OFFICERS

P. S. Howe, Jr., *President*
Sydney M. Cone, Jr., *Vice-President*
Donald H. Powers, *Treasurer*
P. C. Alford, Jr., *Secretary*

BOARD OF TRUSTEES

F. Eugene Ackerman
Norman C. Armitage
A. G. Ashcroft
Earl E. Berkley
André Blumenthal
Joseph H. Brant
W. Hale Charch
Sydney M. Cone, Jr.
Harry L. Dalton
Gaylord Davis
L. K. Fitzgerald
Charles S. Fowler
Milton Harris
Thomas G. Hawley, Jr.
Bertrand W. Hayward
M. Earl Heard
Percival S. Howe
W. A. Karl
Richard T. Kropf
Jules Labarthe, Jr.
Elsie Murphy
Russell B. Newton
F. Everett Nutter
Edward T. Pickard
Donald H. Powers
W. Bailey Sellars
Leonard Smith
Russell C. Smith
A. M. Tenney
Harold J. Walter
Richard D. Wells
Kenneth Wilson

DIRECTOR

John H. Dillon

DEPARTMENT HEADS

James H. Wakelin, *Director of Research*
P. C. Alford, Jr., *Administrative Assistant to Director*

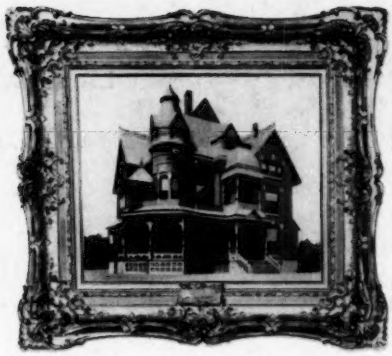
Julian S. Jacobs, *Director of Publications*
10 East 40th Street
New York 16, N. Y.

Edward T. Pickard, *Advisor on Economic Research and Education*
Kent, Connecticut

GENERAL RESEARCH ADVISORY COMMITTEE

Bruce B. Allen
William D. Appel
Norman C. Armitage
A. G. Ashcroft
John L. Bitter
Joseph H. Brant
W. Hale Charch
Kenneth V. Chase
H. D. Corkum
Joseph C. Elgin
J. B. Goldberg
Martin H. Gurley
Walter J. Hamburger
Milton Harris
Thomas G. Hawley, Jr.
M. Earl Heard
George H. Hotte
H. Y. Jennings
Robert M. Jones
Richard T. Kropf
G. K. Lake
Donald H. Powers
E. W. Rugeley
Walter M. Scott
W. A. Sisson
Leonard Smith
R. Hobart Souther
Hugh S. Taylor
Werner von Bergen
Richard D. Wells

Today's fabrics must be different, too!



LOOKING at the past is often amusing. Living in it can be sheer folly. For the world has changed—more people travel, more wives are working, and families are larger. That means people are busy! And busy people haven't time for tedious clothes care. That's why today's customers are looking to you for textiles that combine beauty and practicality.

Du Pont's modern-living fibers give *your* fabrics many care-free extras like wrinkle resistance, pleat and shape retention, easy washing, speedy drying and a minimum of ironing—advantages keyed to the needs of modern living.

Look to Du Pont's know-how in fiber research and fabric development to help you profit from the demands of today's market. Depend on it to help you keep pace with the changing needs of tomorrow.

DU PONT
REG. U.S. PAT. OFF.

BETTER THINGS FOR BETTER LIVING
. . . THROUGH CHEMISTRY

DU PONT'S MODERN-LIVING FIBERS

NYLON) RAYON) ACETATE) ORLON® ACRYLIC FIBER) DACRON® POLYESTER FIBER)